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THE ROLE OF FREE HYDROCHLORIC ACID IN THE LOW-COST REGENERATION OF FERRIC CHLORIDE ETCHANT BY OXYGEN GAS

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Abstract

This thesis concerns the development of a low cost and environment-friendly method for the regeneration of the most widely used aqueous etchant, ferric chloride, found in photochemical machining (PCM) facilities.

In order to implement the above process a comprehensive and automated chemical analysis and control system was designed to fully investigate the key parameters which previous research has suggested play a major role in the analysis of ferric chloride. Monitoring methods have been developed and deployed in a commercial environment such that the etchant could be analysed remotely across the business network or via the internet. This level of monitoring has removed much of the 'black art' previously associated with etching and has allowed proactive control of the etchant and the PCM process in general.

Detailed analysis of the data captured has resulted in a clear understanding of the role the free hydrochloric acid (HCl) level plays in prolonging the life of the etchant. By keeping the free acid level high, dissolved metals remain in solution. The regeneration uses oxygen from the air, combined with surplus HCl, to regenerate the etchant within the etching machine itself. This environment-friendly system has allowed etching to continue in a very controlled way for nearly one year, during which time some 500kg of metal have been dissolved. This has totally eliminated the need to change the etchant which otherwise would have been carried out every 16 weeks. The saving to the sponsoring company has been over £7000 per year.

These combined activities are considered as a major advancement in knowledge and will be of considerable benefit to the PCM industry in general. The monitoring systems alone would significantly benefit any PCM company by reducing rejects and improving product quality and productivity.

Acknowledgments

I would like to express my thanks to Tecan for its support both in financial terms and also for allowing me to conduct such detailed and long term experimental work on production equipment. My particular thanks go to Mr Paul Cane for his continued support and encouragement. I would also like to thanks all my colleagues at Tecan for their understanding, advice and support during the research. I would like to especially thank the following for their specific assistance, Malcolm Andrews for his input in the monitoring systems, Debbie Knapman and her colleagues in the chemical Laboratory, the maintenance team for their help with manufacturing various items of equipment.

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Symbols and Abbreviations

%	Percentage
Bar	Measurement of pressure – 1 bar = 10^5 N/m^2
BEAC	Balanced Etchant Analyser Controller
E	The oxidation reduction potential (ORP) of the solution
E^0	Standard electrode potential – in volts
EDM	Electrical discharge machining
EMS	Environmental management system
Kg	Kilogramme
KWh	Kilowatt hour
l	Litre
mS/cm	Conductivity measurement (micro Siemens /centimetre)
mV	Millivolt
°Bé	Baumé, concentration of solution in terms of specific gravity
ORP	Oxidation reduction potential
PCB	Printed circuit board
PCM	Photo chemical machining
PCMI	Photo Chemical Machining Institute
PEF	Photo electroforming
pH	Acidity measurement = $-\log_{10}[H^+]$
PVC	Polyvinylchloride
Ra	Specific measurement of surface texture determining the average roughness across a sample, usually expressed in µm
RH	Relative humidity
SCADA	Supervisory Control and Data Acquisition
STEL	Short term exposure limit
T	Temperature
µm	Micrometre

Chemical Symbols

Ag	Silver
Al	Aluminium
C	Carbon
Cl	Chlorine
Cr	Chromium
Cu	Copper
Fe	Iron
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
$FeCl_2$	Ferrous Chloride
$FeCl_3$	Ferric Chloride
H_2O	Water
HCl	Hydrochloric Acid
Mo	Molybdenum
N	Nitrogen
Na	Sodium
Ni	Nickel
O	Oxygen
S	Sulphur
Si	Silicon

1 General introduction

1.1 Introduction

Photochemical machining (PCM) also known as photoetching, photofabrication or photochemical milling is a non-tradition manufacturing process used to produce parts from thin flat metal. It uses a combination of photographic masking techniques, resist coating methods and etching to remove unwanted metal to produce the desired part. It has been shown that the process offers a considerable economic advantage over its rival processes of wire erosion, precision stamping and laser beam machining, particularly for small batch sizes of complex parts [Allen 1984, Allen 1986; Allen et al 1989]. By far the most common etching solution in use in the industry is an aqueous solution of ferric chloride $(FeCl_3)$ which is normally operated at a temperature of 50^0C and it has been estimated that around 90% of PCM companies use this solution. The popularity of this solution is due to the fact that it is relatively cheap, can etch a wide variety of metals and is comparatively innocuous when compared with other acid solutions. The most common material being processed by PCM companies is stainless steel although the process is capable of etching a wide variety of metals.

1.2 History of the photochemical machining process

The origin of the process can be traced back to 400 BC when organic acids, such as citric acid and lactic acid, were used to etch metal to form decorative items [Harris, 1974]. Many items of armour have been found from the fifteenth centuries which have etched patterns and old English manuscripts have been found which detail the process of masking with wax prior to acid dipping. The next major change in the process took place in the 19^{th} Century with the development of photography and the production of photo-imagable resists. Prior to this time, masking compounds had been scribed to remove the unwanted area prior to etching and some of this type of etching is still undertaken. This process is known as chemical milling. In the 1950s Kodak

developed the first photoresist suitable for production use, named KPR. This was widely used in the industry from the late 1960s until the development of dry film based photoresists in the early 1970s. Since then, the development of photoresists and manufacturing equipment have turned photochemical machining into a viable alternative manufacturing process, with numerous manufacturing companies now operating world-wide. These companies produce a diverse range of products from decorative items to parts used in space and medical applications in a wide range of metals. It was estimated that the world wide market was worth in the region of $6000m in a survey conducted in 2000 [Allen 2002], and the largest part of this being in the production of TV shadow masks. Much of the recent development has been led by advancements in PCB manufacture, which uses largely similar technology, but photochemical machining continues to push the boundaries of fine line etching far beyond what is currently achieved in PCB production. An example of typical parts is shown in Figure 1.1

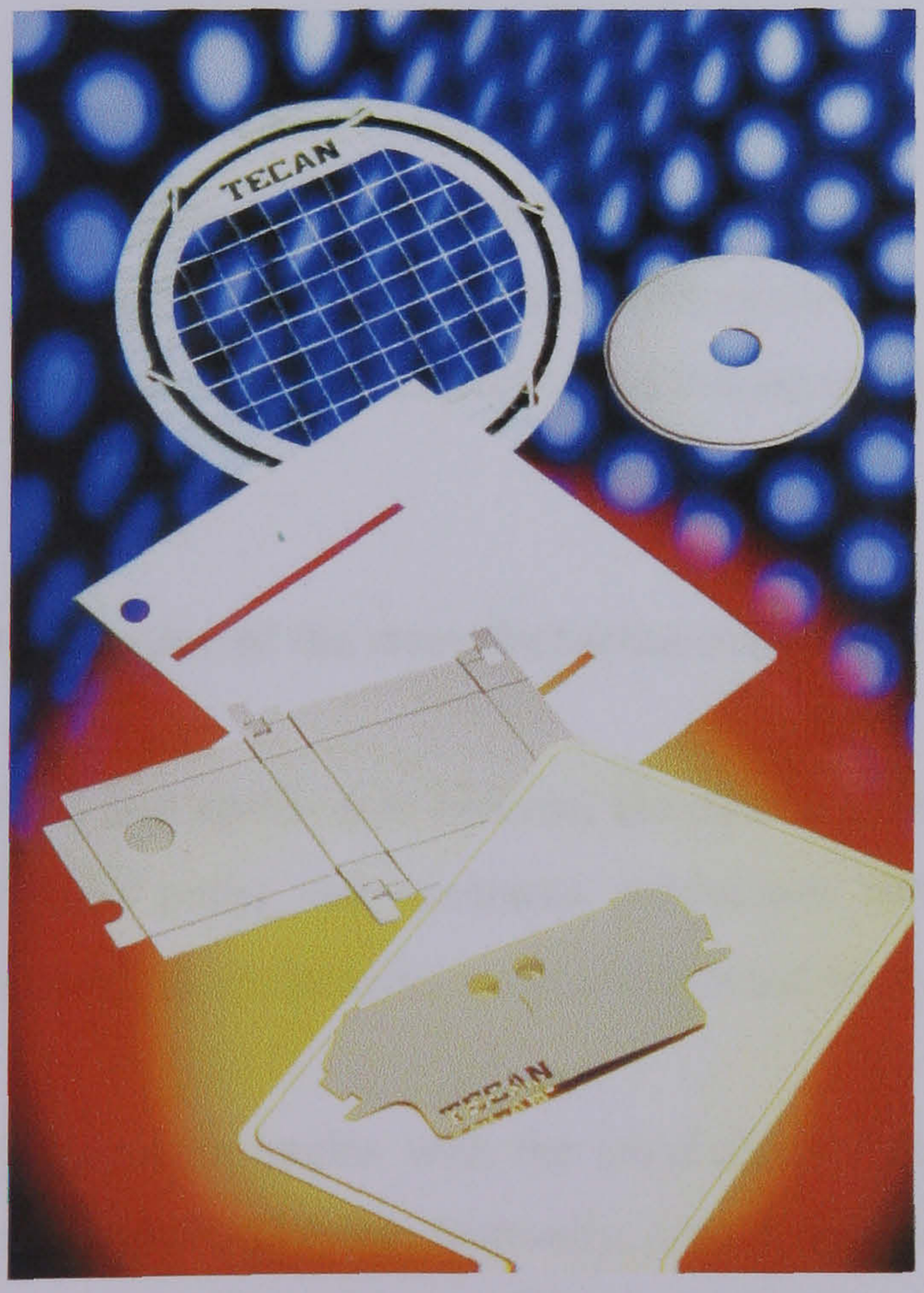


Figure 1.1
Typical parts produced by the photochemical machining process (courtesy of Tecan ltd. – the smaller circular part measure 25mm diameter)

1.3 Advantages of the process

The PCM process offers a number of advantages over conventional metal removal methods. These include:-

- The process does not physically affect the base material. It does not induce stress or cause burrs which could affect the final product.
- The low cost and fast speed of tooling production makes PCM ideal for fast prototype work. This is particularly relevant in today's electronic market where designs change rapidly, and, the 'time to market' is a key factor in the successful marketing of new products.
- Many different types of material can be etched. However, very aggressive and potentially dangerous etchants may be required to etch the more corrosion resistant materials. Details of the metals etched; their properties and the etchants used are given in Appendix 1.
- The hardness of the metal does not affect the etching process as it would with conventional machining.
- Complex shapes do not represent any limitations to the process as would be the case with conventional press tools, the manufacture of which often require detailed and expensive machining and fabrication.

1.4 Outline of the manufacturing process.

PCM is a multi-stage process, the outline of which is given in Figure 1.2. It has two distinct paths, the phototool production and the metal preparation. These come together at the imaging stage and proceed to produce the finished part.

The process begins with the generation of design data suitable for use in the next stage, photo-plotting. Normally, data is received electronically and is manipulated in computer aided design packages to add etch allowance (an offset of the cutting line to

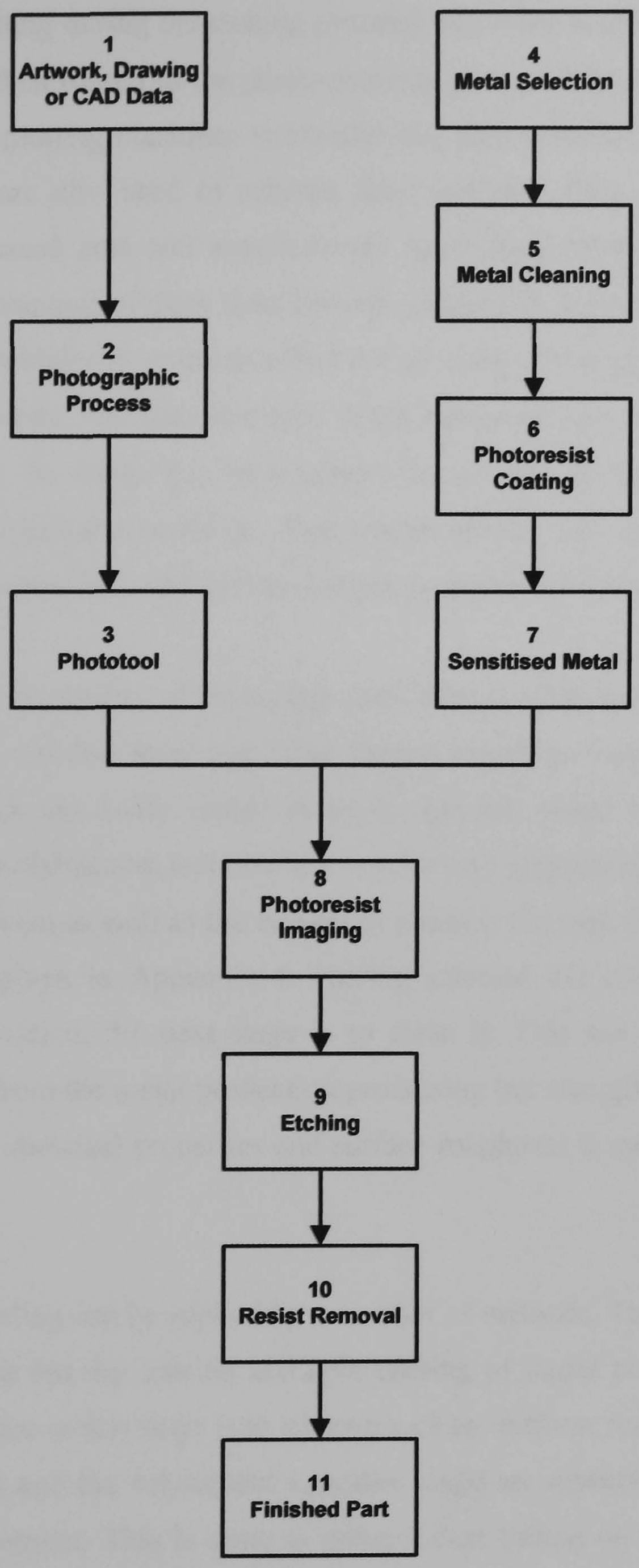


Figure 1.2 Flow chart showing the steps of the PCM Process

allow for undercutting during the etching process) and other features such as holding tags. This data is then passed to the photo-processing stage. Many companies use in-house laser photo-plotting machines to transfer this data onto the photographic film. Glass phototools are also used to achieve finer tolerance parts, but this carries a considerable increased cost and requires very specialised plotting and processing equipment. The advantage of glass is its inherent stability to temperature and humidity variations both of which can seriously affect the accuracy of the more commonly used polyester film substrate. The characteristics of the various phototool types are given in Appendix 2. Once the image has been printed on the film or glass it is developed using normal photographic methods. Two pieces of film are normally made and aligned to form an envelope with the two images accurately registered.

The PCM process is capable of producing parts from a wide variety of metals; the most common are stainless steel and other ferrous metals as well as copper and its alloys, all of which are easily etched in ferric chloride. Some of the more exotic materials such as molybdenum and titanium require very aggressive etching or the use of an electrical current as well as the etchant to produce the part. Details of materials and etchants are given in Appendix 1. Having selected the material to meet the component specification, the next stage is to clean it. This not only removes any contaminants left from the metal production processing but also gives a surface finish which in terms of chemical properties and surface roughness is capable of accepting the photoresist.

The photoresist coating can be applied by a number of methods. The most common is dry film lamination but dip coating and spin coating of liquid photoresists are also used. The importance at this stage is to achieve a clean uniform resist layer. Both this part of the process and the subsequent exposure stage are normally carried out in a clean room environment. This is done to prevent dust falling on the product which would form minor defects as the part is etched.

Two generic types of liquid photoresists are used, known as positive and negative working. In the negative type, the black areas on the phototool correspond to those

areas which need to etched away. At the exposure stage, the high intensity UV light cross links the polymers to form a very tough structure which makes it less likely to be damaged during subsequent process stages. The masked areas are washed away during development and are dissolved away during etching. Negative working resists are more common, accounting for around 90% of the resist used.

Positive working resists operate in the reverse way, the black areas on the phototool representing those areas which correspond to the final part. The positive working resist offers higher resolution capabilities, due in the main to the reduced exposure energies required to polymerise the resist. But they do tend to be more brittle so can easily be damaged. Figure 1.3 shows a comparison of the two resist types during the key process steps.

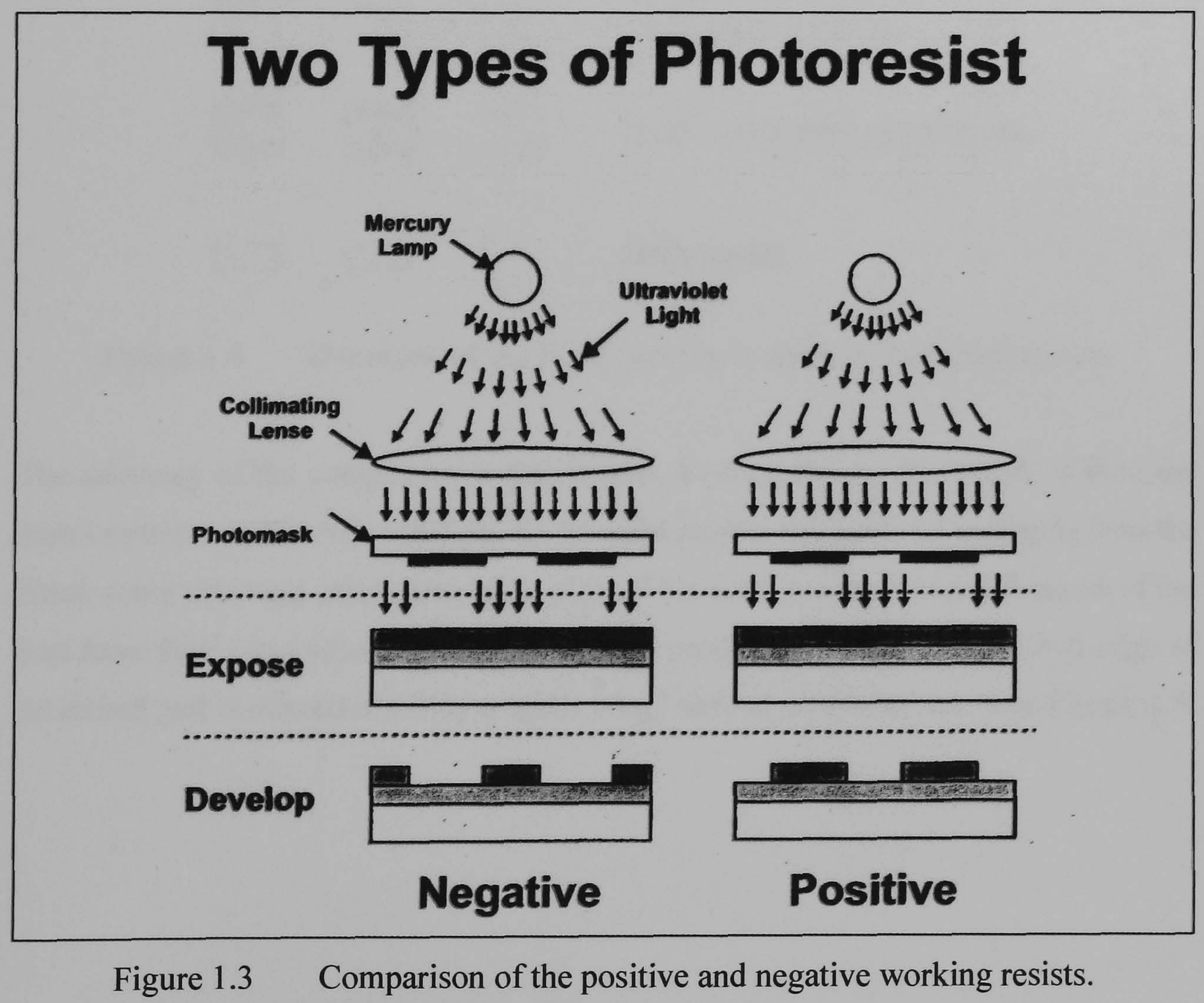


Figure 1.3 Comparison of the positive and negative working resists.

The imaged blanks of material are then passed through an etching machine which sprays acid (normally ferric chloride) at the surface. This dissolves away the material that is not required. This process is usually done from both sides to speed up the process and ensure a uniform edge profile. Figure 1.4 shows the key stages in the imaging and etching process.

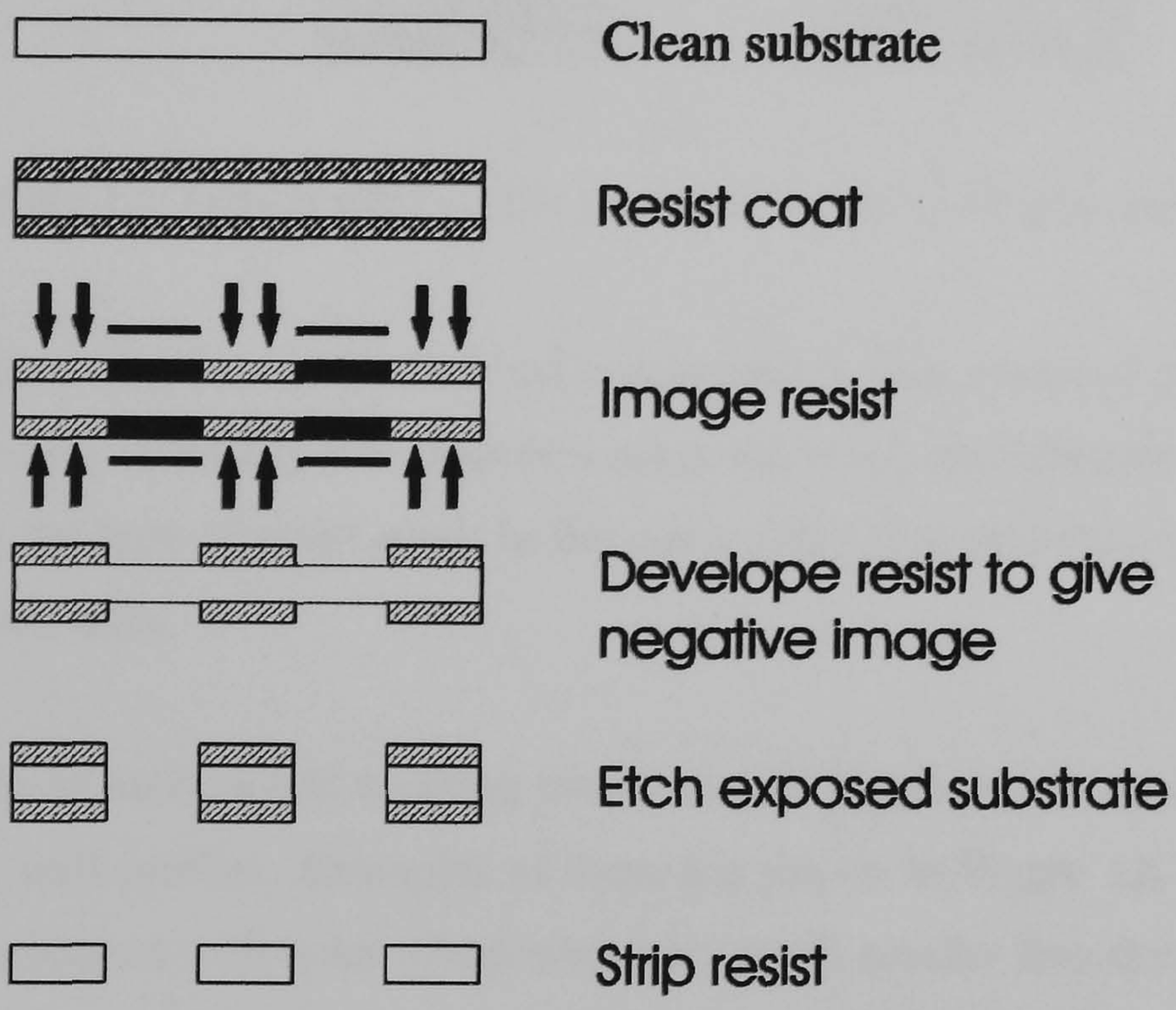


Figure 1.4 Overview of the PCM process in terms of part manufacture

The accuracy of the component is determined, in the main, by the length of time the metal remains in the etch solution. As the acid attacks the material vertically into the blank some sideways attack also takes place. This is the reason why the features of the part have their sizes adjusted at the photo-tool production stage. The finished edge of an etched part is characterised by a 'gulls wing' shaped profile as shown in Figure 1.5.

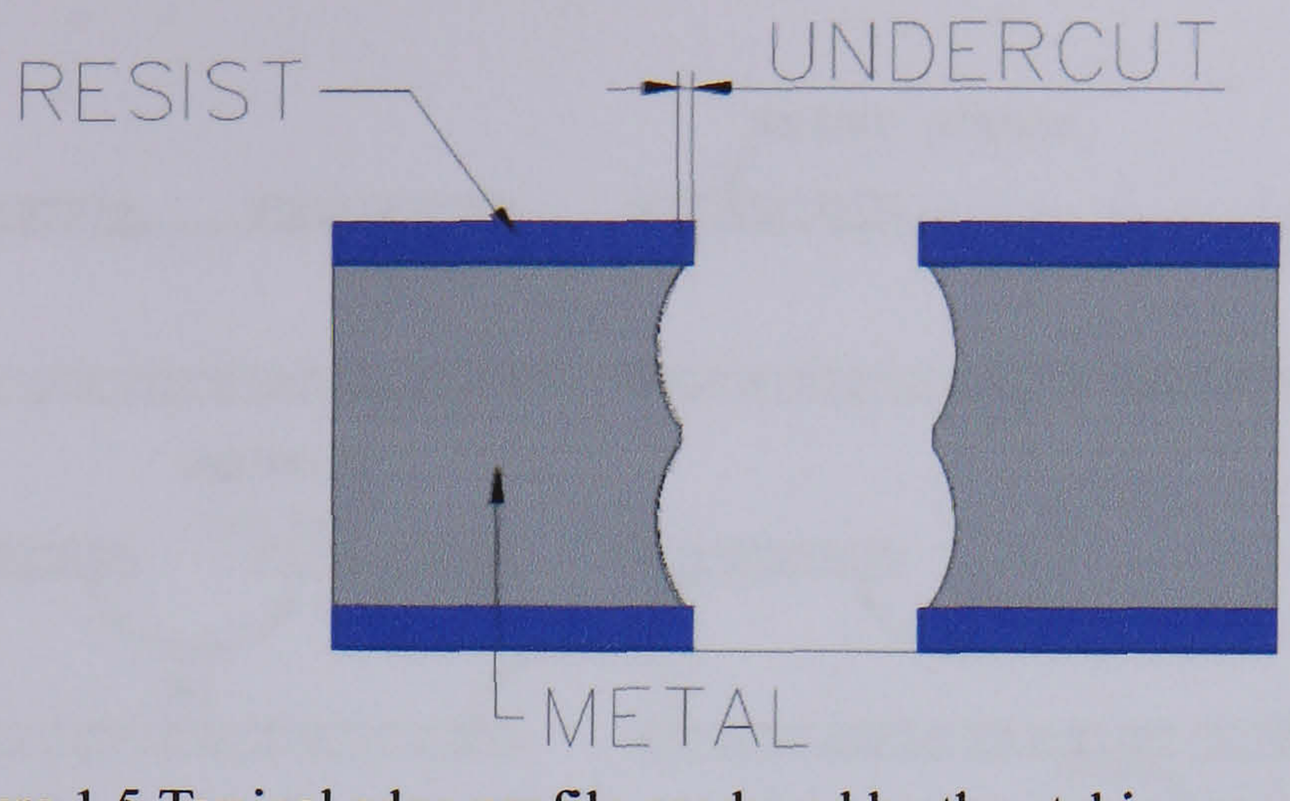


Figure 1.5 Typical edge profile produced by the etching process

The resist which remains on the finished component is then removed in a stripping process. This uses chemistry that dissolves away the resist, the selection of which is dependent on the type of resist used. In the case of dry film photoresist this will be based on caustic soda.

Using a variety of etching and masking processes it is possible to produce parts with different side wall profiles. Examples of these are shown in Figure 1.6. In this way parts can be produced with holes of diameter very much smaller than the thickness of the metal. This is particularly important when producing sieves and optical components.

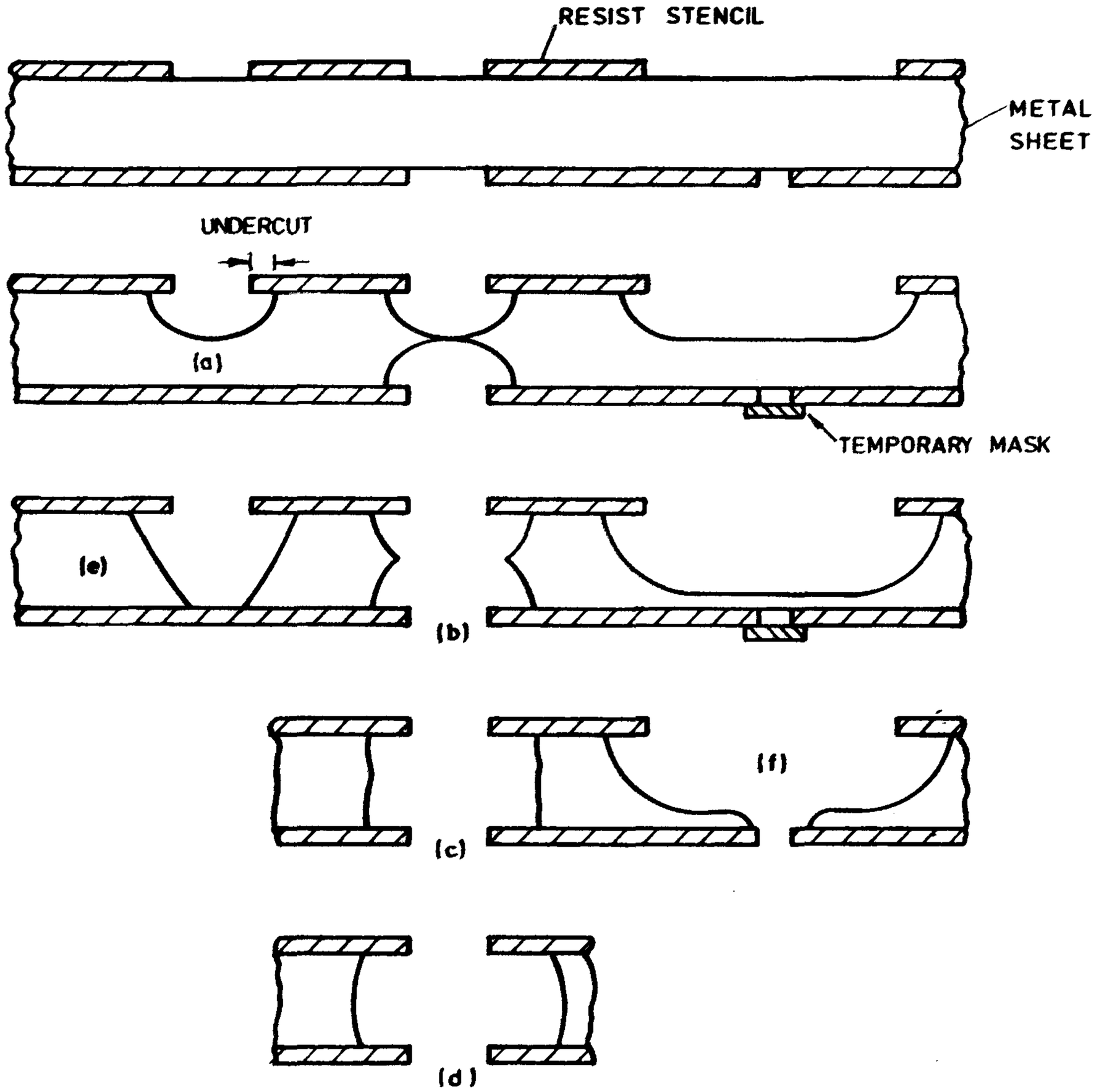


Figure 1.6 Typical etch profiles achieved by the PCM process [Allen, Almond and Bridges 2005]

1.5 Future development of the process

Many developments are taking place, driven mainly by the need for increased productivity and increased product quality. The most notable of these are increases in the level of process control and enhancements in the design and automation of the process equipment. One of the major developments in PCM at the current time is centred around the development of imaging systems and in particular laser direct

imaging (LDI) and ink jet printing processes which could potentially remove the photographic steps totally.

1.6 Competing technologies

There are numerous other manufacturing processes which are also used to produce metal parts. Of particular interest are those which directly rival PCM in terms of cost and ability to manufacture complex 2D shapes. Table 1.1 gives an overview of some of these processes detailed below.

- **Laser cutting** has advanced considerably over the years and is capable of producing complex parts in a wide variety of materials. It has the advantage of not using any chemicals and the number of process steps is reduced. However, machine capital costs are high and parts can be affected by a localised heat affected zone around the cut edge. Production cost is directly related to the length of the cut edge and for this reason is more expensive than PCM when batch sizes progress beyond prototype production.

- **Precision stamping** is an obvious method which competes with PCM. However, tooling costs are normally very high and therefore the process is only normally used for high volume production. The tolerance and accuracy of this process is becoming ever finer. However, PCM still remains capable of resolving finer detail.

- **WEDM** (wire electric discharge machining) uses an electrically energized thin brass wire to slice through metal - including difficult-to-machine metals. The wire EDM machine, an example of which is shown in Figure 1.7, uses rapid, controlled, repetitive spark discharges. The edges produced are smooth but matte, typically with a surface finish between 0.4 and 1.63 micrometres. The edges of the finished work piece will have virtually no burrs. The work piece is moved in relation to the fixed wire by CNC control. Capital equipment costs are high, due to the complex control system used to move the work piece and

generate the spark. The cost of the process is directly related to the length of cut and this makes it more expensive than PCM, particularly when batch sizes increase.

Figure 1.7

Typical Wire EDM machine

- **Water jet cutting** in this process a stream of pressurized water passing through a tiny hole is used to cut almost any material. In some cases the stream is assisted by abrasive material. An abrasive stream is much more powerful than pure water jet and it is this system that is normally used for metal cutting. The use of CNC movement ensures that high cutting accuracy is achieved and the process leaves a burr-free edge with no heat affected zone as is often the case with laser cutting. The production cost is directly proportional to the length of cut and for this reason the process tends to be more expensive than PCM for all but the lowest batch volumes.

- **Photo electroforming (PEF)** is very similar in many respects to PCM; many of the process steps are, in fact, the same. But instead of etching to remove metal, metal is electrodeposited into the mould made by the resist patterning process. The process is more expensive then PCM but is capable of producing parts with very fine detail and improved edge profiles. See Figure 1.8.

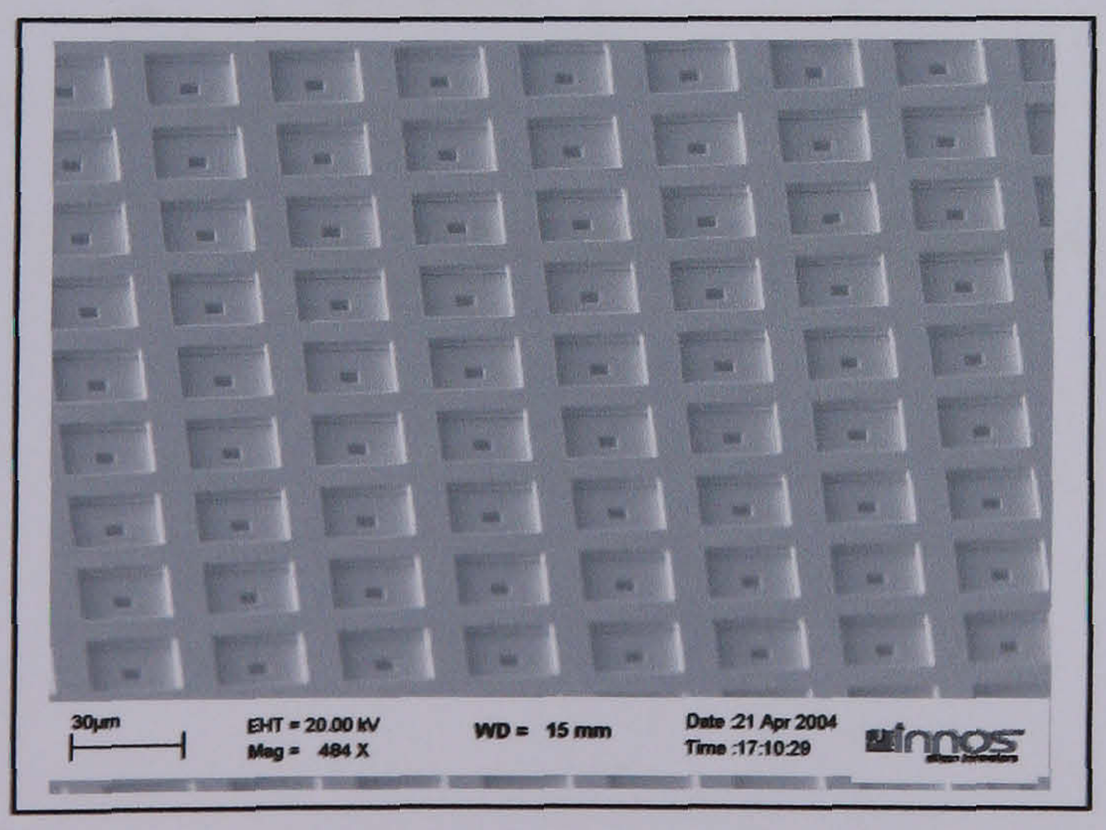


Figure 1.8

Typical PEF parts produced by Tecan

Process	Tolerance	Typical material thickness		Compatible materials	Typical batch sizes
		Min	Max		
Laser cutting	+/- 10 µm	25 µm	3 mm	Most metals, Plastics, Ceramics	Small to medium
Precision Stamping	+/- 10% material thickness	50 µm	5 mm	Most metals	Very large
Wire EDM	+/- 10 µm microns	25 µm	300 mm	Any conductive metal	Small
Water Jet	+/- 10 µm microns	25 µm	100 mm	Most metals, Plastics, Fabric, Stone and wood.	Small to medium
PEF	+/- 5% material thickness	10 µm	100 µm	Nickel, copper and some precious metals	Small to medium
PCM	+/- 10% material thickness	25 µm	3 mm	Most metals (some may need special etchants)	Small to medium

Table 1.1 Key aspects of the various competing technologies

1.7 Tecan Limited

The majority of this research was carried out at Tecan Ltd. in the United Kingdom. Tecan has been established for 35 years and specialises in the photoetching of fine parts for the electronics industry. The plant consists of two clean rooms, for the imaging of the material, together with a range of etching and other conveyorised equipment for the pre-treatment and finishing of components. Historically Tecan had used sodium chlorate and hydrochloric acid to regenerate acid but during the course of this study it introduced chlorine as well as the oxygen-based system which this study covers.

1.8 Environmental issues

During recent years there has been an ever increasing awareness of the environmental impact which manufacturing industry is having on our natural world. This has led to the introduction of numerous pieces of legislation. Whilst legislation is not new, the UK was one of the first to introduce controls passing the Alkali Act in 1863. The effect such legislation is having on businesses around the world is becoming ever more severe [Ler 1998]. The Environmental Protection Act 1990 is the primary article of legislation under which UK companies have to operate. This aims to reduce emissions and minimise environmental impact by the use of 'best techniques not entailing excessive cost' and constant risk assessment. The legislation is policed by the Environment Agency who has the authority to issue prohibition notices and prosecute offending companies who do not adhere to the act.

Many companies operate an Environmental Management System (EMS) to ensure compliance with the law. To assist in this, and demonstrate their level of commitment to environmental issues, some pursue accreditation to the ISO 14001 standard. This operates in a very similar way to the Quality standard ISO 9001.

The process of PCM uses chemicals at nearly all stages of its use; the environmental impact of the process is therefore considerable. In this study only the effects of the use and disposal of the ferric chloride etching solution will be considered.

The main issues associated with the use of ferric chloride are;

1. There is an obvious impact of the purchase of new ferric chloride; both in terms of the manufacturing process for producing the solution and the environmental affect of having to transport it from the manufacturing site to the company. Currently ferric chloride costs between £0.45 and £0.18 per litre dependent on volume.
2. The spent ferric chloride has to be disposed of in a controlled way to meet the requirements of the various pieces of legislation. In the main, companies dispose of it either by treating it in an effluent treatment plant to produce a "cake" from a filter press which is then sent to landfill sites or by sending the liquid for recycling. Both of these options are becoming increasingly more expensive, due to the increasing costs of road haulage and the reduced number of landfill sites which will accept this type of waste. The latter has come about as a result of new legislation which came into effect in July 2004 and restricted the number of land-fill sites which can take hazardous waste. Waste material sent to land fill also attracts a 'land fill tax', which is currently in the region of £20/tonne. This cost is certain to rise in the coming years.
3. If etching solutions are changed at a frequent rate there is an increased risk of spillage which if uncontrolled can affect water courses.
4. For health and safety reasons, when solutions are changed the process normally happens at room temperature, therefore additional costs and environmental impact will result from the cooling and heating required to facilitate the change

The use of regeneration to prolong the useful life of a batch of etchant has considerable advantages in reducing the environmental impact of the process [Allen,

Ler 1999]. But, as will be shown in chapter 2, the regeneration systems themselves have an environmental impact due to the chemicals used. This is one of the main drivers for studying the use of oxygen as an environment-friendly alternative method to regenerate the spent solution.

1.9 Objectives and Scope of the Thesis

Previous research by Cranfield students [Ler (MSc) 1993, Ler (PhD) 1998 and Peters (MSc) 1999] has shown that oxygen has the potential to regenerate ferric chloride etchant. Some of this work was laboratory-based at Cranfield and some was industrially based, at Tecan, but no long-term testing has ever been undertaken. A patent does exist [Lubert 1993] but no technical/economic data has been revealed by the literature search to determine whether the process was economic or otherwise. This study aimed to undertake prolonged testing in a true industrial situation with a view to determining its true commercial potential and compare it, technically and economically, with other regeneration methods currently in use both at the sponsoring company and around the world.

All of the other systems used for regeneration have a significant environmental impact. Many use extremely hazardous chemicals which also pose significant health and safety problems. The use of oxygen would reduce such hazards and generally improve the environmental image of the PCM industry.

The previous work of Peters indicated that the process was very inefficient, calculating the efficiency as a mere 3.55%. A detailed review of the experimental setup has suggested that improvements to the acid injection and mixing systems may significantly increase the overall process efficiency. This research aimed to investigate, in particular, the effect of changes in the configuration of static mixer and chemical feed points. Together with studies of the timing of chemical additions relating to the parameters of the etchant as it changes during the production process.

The long-term aim of the study was to investigate if an oxygen regeneration system could be made commercially available to the PCM industry for ferric chloride etching solutions.

Since air contains 21% oxygen it was considered that the use of compressed air, as an alternative to compressed oxygen used in the previous research, could prove successful. Whilst it is obvious that significantly more air would be required, it was felt that this could prove very economical since the cost of compressing air and delivering it to the machine is much lower than that associated with the use of compressed oxygen. No record of any previous work having ever been undertaken in this area has been found so it was felt that this would be a significant contribution to knowledge.

A large amount of work has previously been carried out in determining what parameters need to be monitored in an etch solution in order to predict its behaviour [Almond and Allen 2004]. No results of long term or real time monitoring of the etching process in an industrial situation have been found and it was felt that such an investigation would be a contribution to knowledge and of considerable benefit to the industry. In order for the PCM industry to move forward technically in a very challenging economic market place it is essential that it adopts some of the principles of data monitoring and process control which other industry sectors have adopted. This study aimed to investigate this and determine if it was technically and economically possible to monitor the etching process in such a way.

A previous survey of PCM companies had been conducted [Ler 1998] and this was compared with a survey carried out during this study with a view to understanding current trends in industry. A detailed economic analysis of the various regeneration systems was also updated and compared with actual results obtained during the experimental work.

2 Technical background, literature survey, and review of industrial trends

2.1 Chemistry of etching

The etching process has been described as controlled corrosion [Allen 1986]. The material to be removed is dissolved by a process involving both oxidation and reduction. In the case of ferrous materials, the material is oxidised by the etchant, normally ferric chloride, to form a soluble ferrous salt.

Chemically, the following reactions occur:

Oxidation of the metal	$Fe \rightarrow Fe^{2+} + 2e^{-}$	E_0=0.44v
Reduction of the etchant	$2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$	E_0=0.771v
Thus, overall	$2FeCl_3 + Fe \rightarrow 3FeCl_2$	E_0=1.21v

In order to ensure that the etchant is able to dissolve the metal, it is essential to ensure that the material's oxidation-reduction potential (ORP) is lower than that of the etchant. So in the above example iron (E_0=0.44v) would etch well. In the case of silver, the byproduct produced is silver chloride which is insoluble in ferric chloride and so would block further reaction, etching would stop. Titanium, which is often used for the construction of parts in etching machines, will not etch at all in ferric chloride due to an insoluble titanium oxide (TiO_2) layer which is formed on the surface. To overcome this, alternative etchants would be used. Typically for silver this would be ferric nitrate. The process of etching reduces the activity level of the etchant. The ferric chloride is reduced to ferrous chloride and, as will be seen in section 3.3, the ORP of the etching solution will fall [Ler 1998]. It is this process that regeneration seeks to reverse.

Numerous methods of regeneration have been well documented [Allen and White 1992]. In all cases the ferrous chloride is converted back to ferric chloride by the addition of some form of oxidising agent. A review of typical methods is given later.

Chemically, the following reactions take place during etching and regeneration (the example shown is for chlorine regeneration. Other systems are described later):

The etching process

$$2FeCl_3 \text{ (Ferric Chloride)} + Fe \text{ (Iron)} = 3FeCl_2 \text{ (Ferrous Chloride)}$$

The regeneration process

$$3FeCl_2 + 3/2Cl_2 \text{ (Chlorine)} = 3FeCl_3 \text{ (Ferric Chloride)}$$

Note that as a result of the regeneration process more ferric chloride has been produce than was initially present.

2.2 Reasons for considering regeneration.

There are four main topics of consideration when reviewing the desire to regenerate the etching solution.

- Cost
- Environmental
- Technical
- Product quality

2.2.1 Cost considerations.

As material is etched into solution the strength and activity level of the solution will decrease and the ORP will fall [Ler 1998]. This will, in turn, reduce the rate at which further material can be dissolved, hence reducing the rate of etching and productivity of the process and increasing manufacturing costs. If no regeneration is installed, a point will be reached at which the solution can no longer remove metal at all. It is extremely unlikely that this final end point would ever be reached in a commercial environment, since other factors such as the poor profile of the etched part and speed of production normally determine the point at which the acid should be changed. Regeneration extends the useful life of the etchant and hence reduces cost [Markle 1986].

Previous work by Allen and Ler [1999] has shown that it is possible to increase the percentage utilisation of the spent solution significantly by regeneration, hence reducing the amount of ferric chloride required to etch a specific volume of material. This is due to the fact that additional ferric chloride will be produced as a result of the regeneration process. This is shown in summary in Figure 2.1

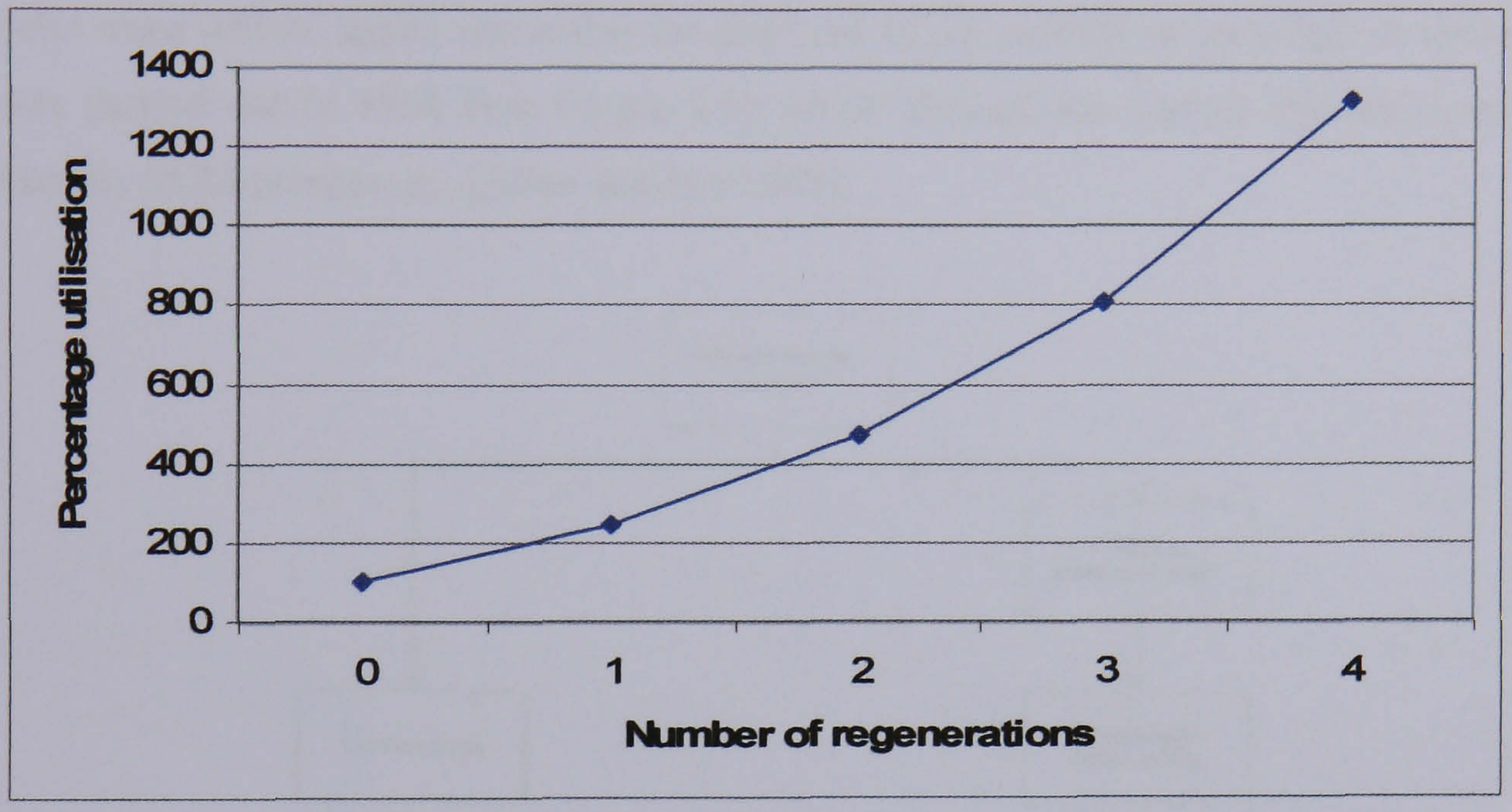


Figure 2.1 Utilisation of ferric chloride when regeneration is used
[Allen and Ler 1998]

The cost associated with changing the etch solution arises from three areas.

- The cost of the new solution.
- The cost of safely and legally disposing of the partially spent solution. As detailed below, disposal costs are an ever-increasing charge as environmental legislation becomes ever tighter.
- The labour charges involved in emptying, cleaning and re-filling the etching machine.

2.2.2 Environmental

With no regeneration the spent ferric chloride will have to be removed from the production facility. Two options are open to companies: either send liquid waste for landfill or recycling, or treat it in-house through effluent treatment plants to produce a solid cake which, again, can either be disposed of by landfill or recycled. A survey was carried out in 1998 (see Figure 2.2) which showed the typical disposal routes used by PCM companies, [Allen and Ler 1999].

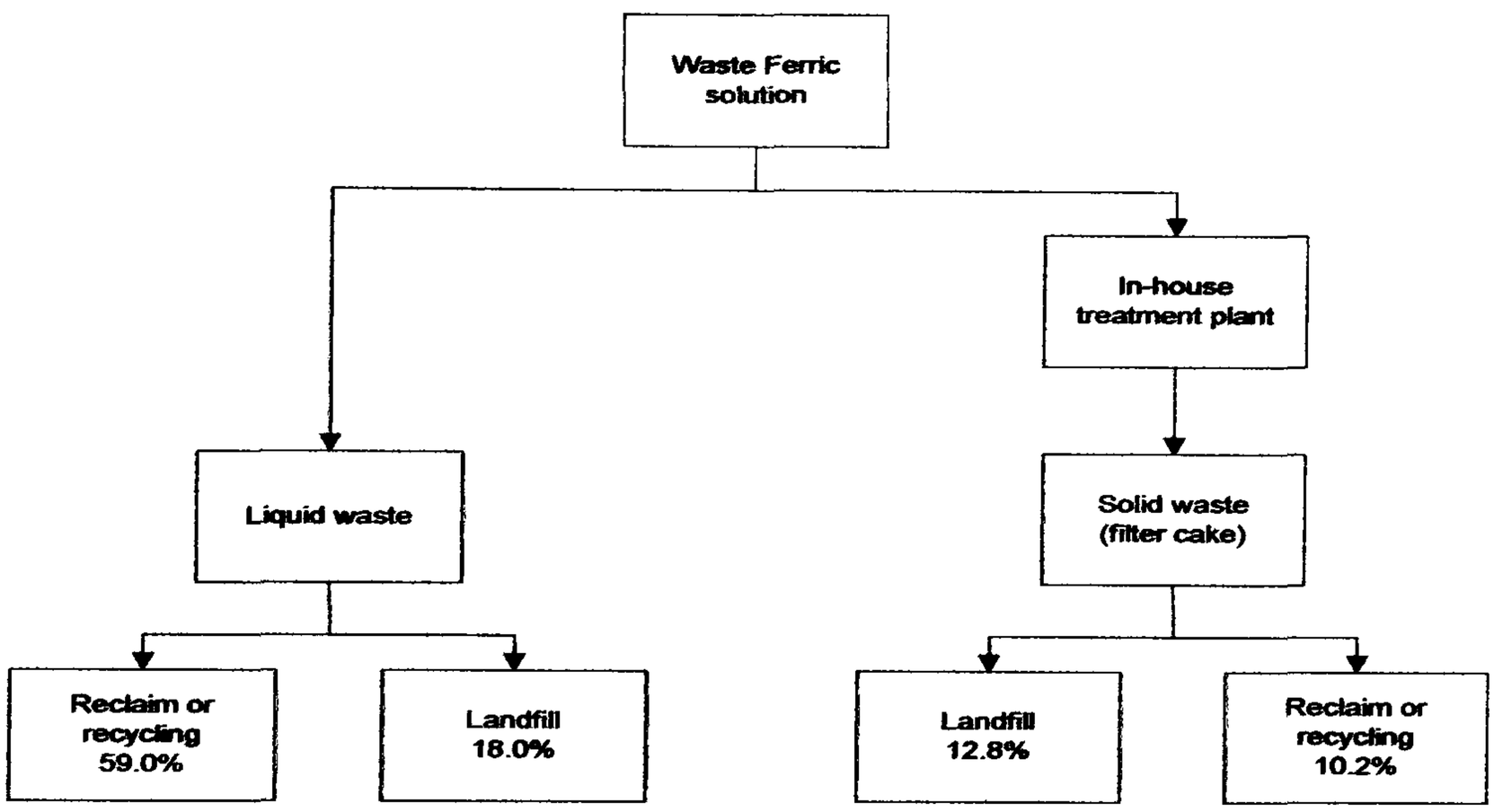


Figure 2.2 Methods or waste ferric disposal [Allen and Ler 1999]

Environmental issues are receiving higher importance in modern industrial facilities. In the UK there are numerous articles of legislation governing the operation of etching plants, in particular the Landfill Directive (revised in 2005). This reduced the number of sites in the UK which could take ferric chloride waste, and in turn increased disposal costs three fold in the one year.

Many PCM companies are considering ISO14001 as an operating standard. A fundamental requirement of this standard is the process of constant review and improvement of the processes within the facility and one way of reducing the impact of the etching process is to regenerate the spent solution. In doing so, the disposal of spent solution is reduced considerably. Replacement is only necessary when the metal

loading of the solution increases significantly. In some regeneration systems methods are employed to minimize this metal loading using filtration, hence increasing the life of the etchant still further [Dorrenbach 1991].

In some cases, where regeneration is carried out on a large scale, the regeneration process itself produces additional ferric chloride which can be used to top up machines or start new machines, thus eliminating the need for additional purchasing and thus reducing the environmental impact associated with the manufacture of fresh chemistry and transport to site. The ferric chloride 'produced' by regeneration will have a level of alloy loading consistent with the material being etched so would usually only be suitable for etching more of that particular material.

It is accepted that there is an environmental impact of producing the chemistry required for the regeneration but overall regenerated solutions have a lower environmental impact. This study looks in particular at the potential use of oxygen for regenerating the spent etchants, considered as one of the most environment-friendly processes.

A survey [Ler 1998] showed that around half the companies taking part carried out some form of regeneration. The main drivers to this appeared to be both economic and the desire to operate in a more environment-friendly way. In fact many of the companies who did not regenerate stated that they would, even if the cost was higher, but lack of technical expertise was preventing them.

2.2.3. Technical

Companies are facing ever-increasing demands on the tolerances and surface finish of parts they are being asked to produce. Figures 2.3 and 2.4 illustrate the increasing complexity and tolerance of parts being produced over the last few decades. As the etch solution becomes depleted, controls over these factors become increasingly difficult to maintain as they are directly related to the condition of the etchant. In an

etching solution that has been regenerated, controls will have been put in place to monitor and adjust the key chemical indicators such as ORP and pH which in turn will bring stability to the process as a whole.

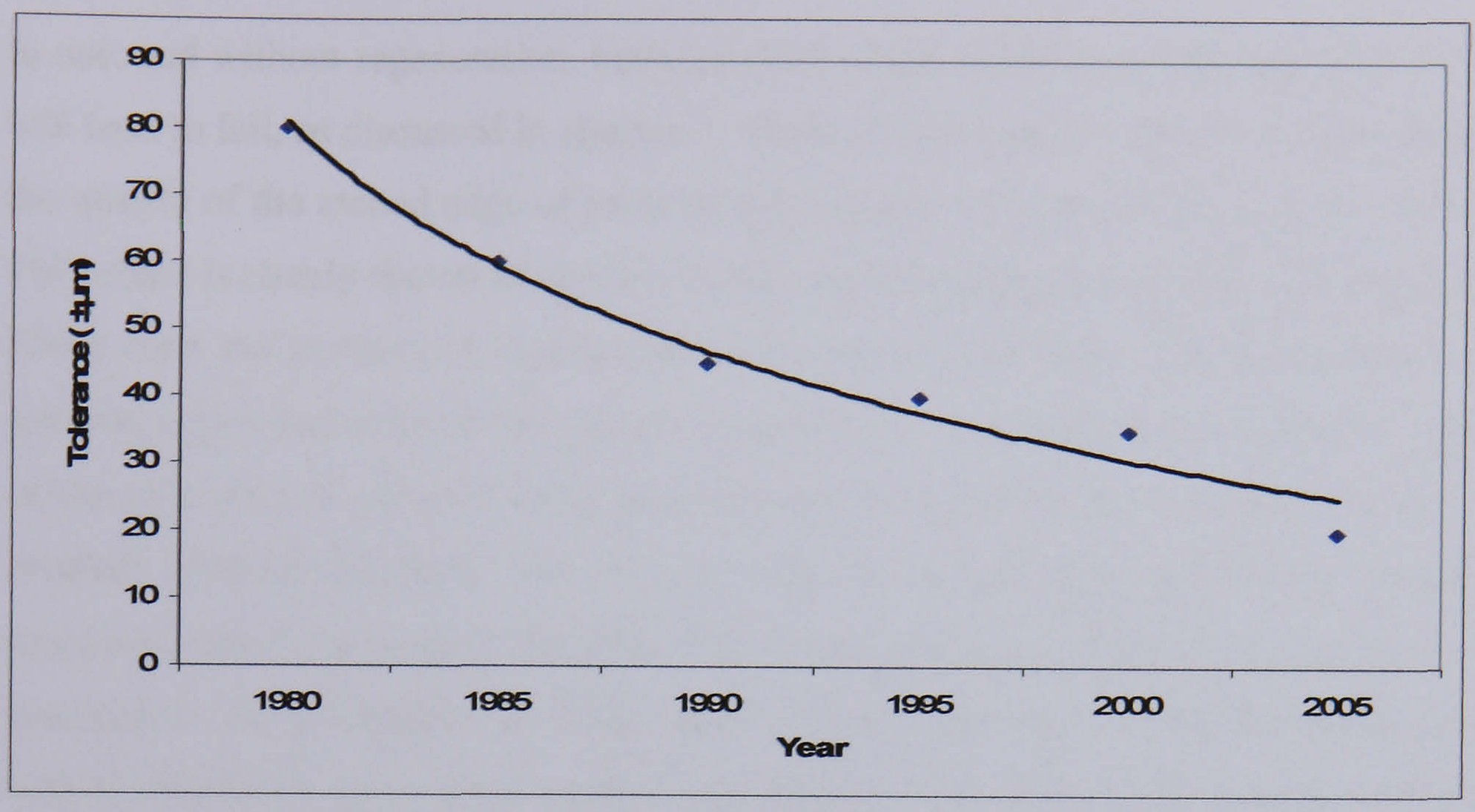


Figure 2.3 Reducing tolerance requirements demanded by customers
[Holland 2003 and Mitsui 2004]

Figure 2.4 Increase in the number of connections on typical lead frame components
[Holland 2003 and Mitsui 2004]

2.2.4 Consistent product quality

In use, and without regeneration, both the ORP of the solution and the free HCl level will tend to fall, as discussed in chapter 3. Both of these are key factors in controlling the quality of the etched edge of parts being produced [Visser and Weissinger 1993]. This effect is clearly shown from studying the two photographs in Figures 2.5 and 2.6. These show the surfaces of part-etched components etched with fresh solution and a solution which had reached the end of its useful life. This same effect would be seen on the side wall of any part being produced and it would be increasingly difficult to maintain product tolerance. The very fact that the etched edge was getting rougher could also make the product unusable. This would be typical of the etching operation involved in the production of solder mask stencils. Here, the definition of the side wall is critical to allow good solder paste release when the stencil is used in PCB production. A good indication of this effect is the measurement of surface finish of any part-etched feature on the artifact. Typically a good surface finish for AISI 316 grade stainless steel would be better than Ra 0.4 μm.

Figure 2.5
SEM image of the surface of an etched part.

This was produced with fresh ferric chloride.

The Ra of this part was 0.25 μm

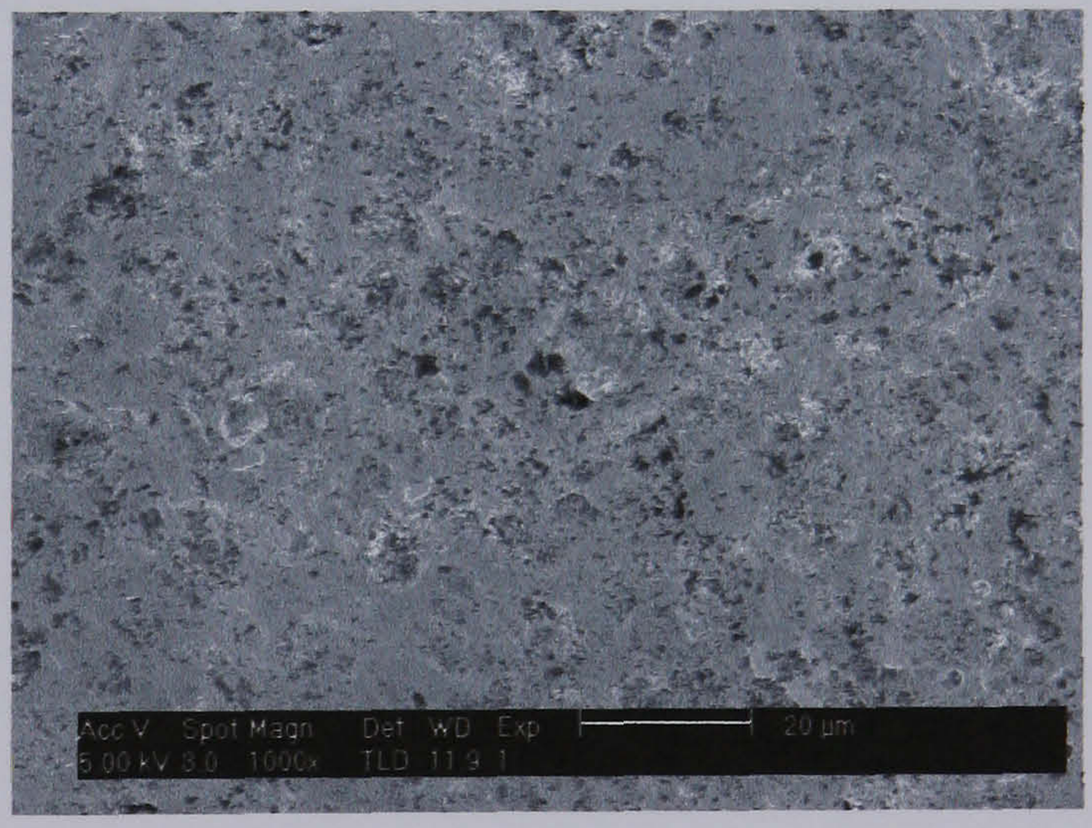
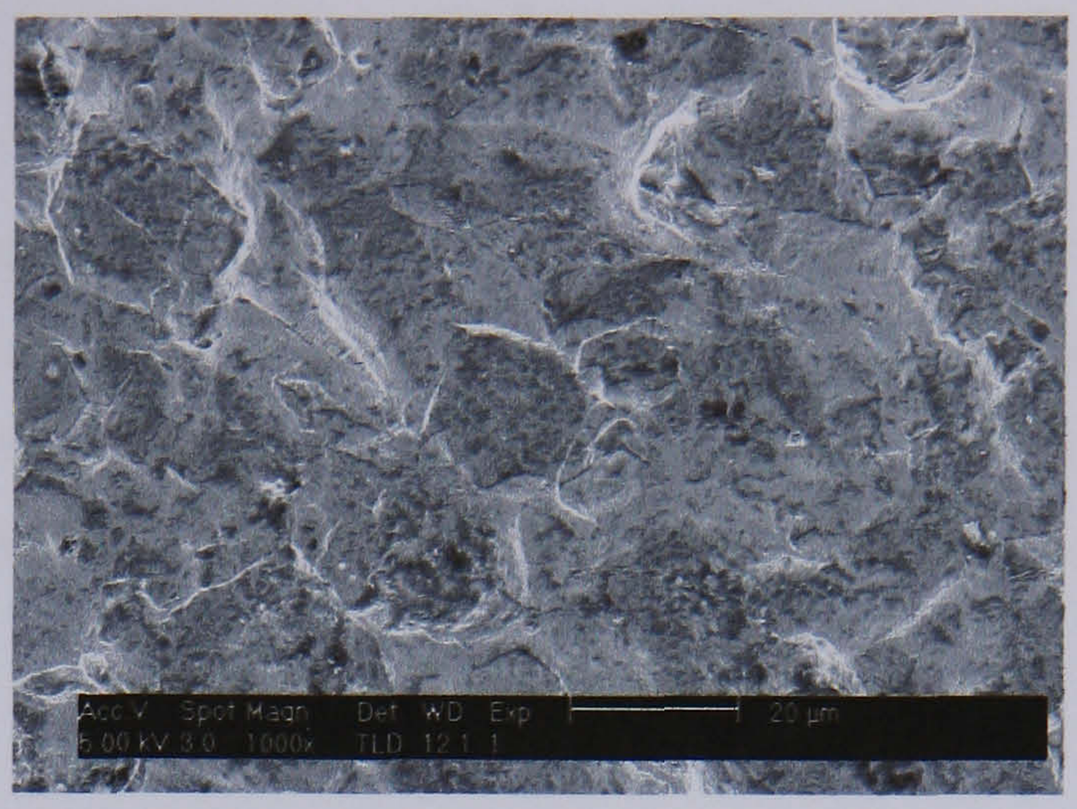


Figure 2.6
SEM image of the surface of an etched part.

This was produced with spent ferric chloride.

The Ra of this part was 14 µm



2.3 Regeneration methods

There are a number of methods for the regeneration of used ferric chloride etchant. These use a variety of chemical or electro-chemical reactions to oxidise the Fe^{2+} (ferrous ions) back to Fe^{3+} (ferric ions). Many of the systems use hazardous chemicals and produce byproducts which can affect the etching solution. Table 2.1 shows the various methods in use and the chemical reactions involved. In the following sections each method is described in detail, together with comments on the advantages and disadvantages of each process. The commercial aspects of the various systems are discussed in section 2.6.

Method	Regeneration additions		Regenerated solution
Chlorine	$3FeCl_2 + 3/2Cl_2$	$\Rightarrow$	$3FeCl_3$
Ozone	$3FeCl_2 + 3HCl + 3/2O_3$	$\Rightarrow$	$3FeCl_3 + 3/2O_2 + 3/2H_2O$
Sodium chlorate / hydrochloric acid	$3FeCl_2 + 3HCl + 1/2NaClO_3$	$\Rightarrow$	$3FeCl_3 + 1/2NaCl + 3/2H_2O$
Electrolysis	$3FeCl_2 + 3HCl$	$\Rightarrow$	$3FeCl_3 + 3/2H_2$
Oxygen	$3FeCl_2 + 3HCl + 3/4O_2$	$\Rightarrow$	$3FeCl_3 + 3/2H_2O$

Table 2.1 Chemical reactions associated with commonly used methods of regeneration

All the theoretical formulae and calculations assume only iron is dissolved into solution during etching. Whilst this is normally not the case, the complex equations which result for considering all the elements are not considered necessary in making the general assumptions and indications which the formulae allow without such additions.

2.3.1 Chlorine regeneration

In this system of regeneration, chlorine gas (Cl_2) is injected into the etch solution. This converts the ferrous ions to ferric ions as shown below:-

$$3FeCl_2 + 3/2Cl_2 \rightarrow 3FeCl_3$$

The very strong oxidising effect of the chlorine makes this one of the most popular methods of regeneration in common use today. Commercial systems are available from a number of sources and a typical design is shown in Figure 2.7 This type of system is used in facilities which dissolve large quantities of metal. This is due to the efficiency of the process which allows fast regeneration.

The hazardous nature of the chlorine gas used requires careful handling and dependant on the amount of gas stored, may require specific local authority approval and special purpose storage facilities [Allen and White 1992].

Figure 2.7

Typical Chlorine regeneration system as sold by Chemcut, typical of equipment used in facilities with high metal through put. Picture courtesy of ChemCut Corporation

Advantages

- Due to the strong oxidising nature of the chlorine this is a very efficient system.
- Commercial equipment is readily available.
- Very cost effective for facilities etching large amounts of metal.
- The regeneration method does not produce any byproducts which would affect the etching solution.

Disadvantages

- Chlorine gas is a very hazardous substance – the short term exposure limit is only 3ppm. [Occupational Exposure Limits 2002, EH40]
- Expensive special storage, handling and monitoring equipment is required.
- In the UK, government legislation tightly controls the use of large volumes of chlorine, particularly in built-up areas.

2.3.2 Electrolytic regeneration

This system relies on the anodic oxidation of the ferrous chloride ion Fe^{2+} to ferric ion Fe^{3+} [Allen 1991]. The reaction takes place in a chemical cell as shown in Figure 2.8 according to the formula:-

$$3FeCl_2 + 3HCl \rightarrow 3FeCl_3 + 3/2H_2$$

In this process the spent solution (Fe^{2+}) is used as the anolyte in an electrical cell. The catholyte is acidified sodium chloride. The two are separated by an ion exchange membrane. When a charge is applied to the cell this membrane allows only negatively charged chloride ions to pass into the anolyte to initiate the reaction at the anode:-

$$Fe^{2+} \rightarrow Fe^{3+}$$

The membrane prevents the positively charged (Fe^{3+}) ions from passing back into the catholyte. Similarly at the cathode the positively charged hydrogen ions are reduced to hydrogen gas.

$$2H^+ + 2e^- \rightarrow H_2$$

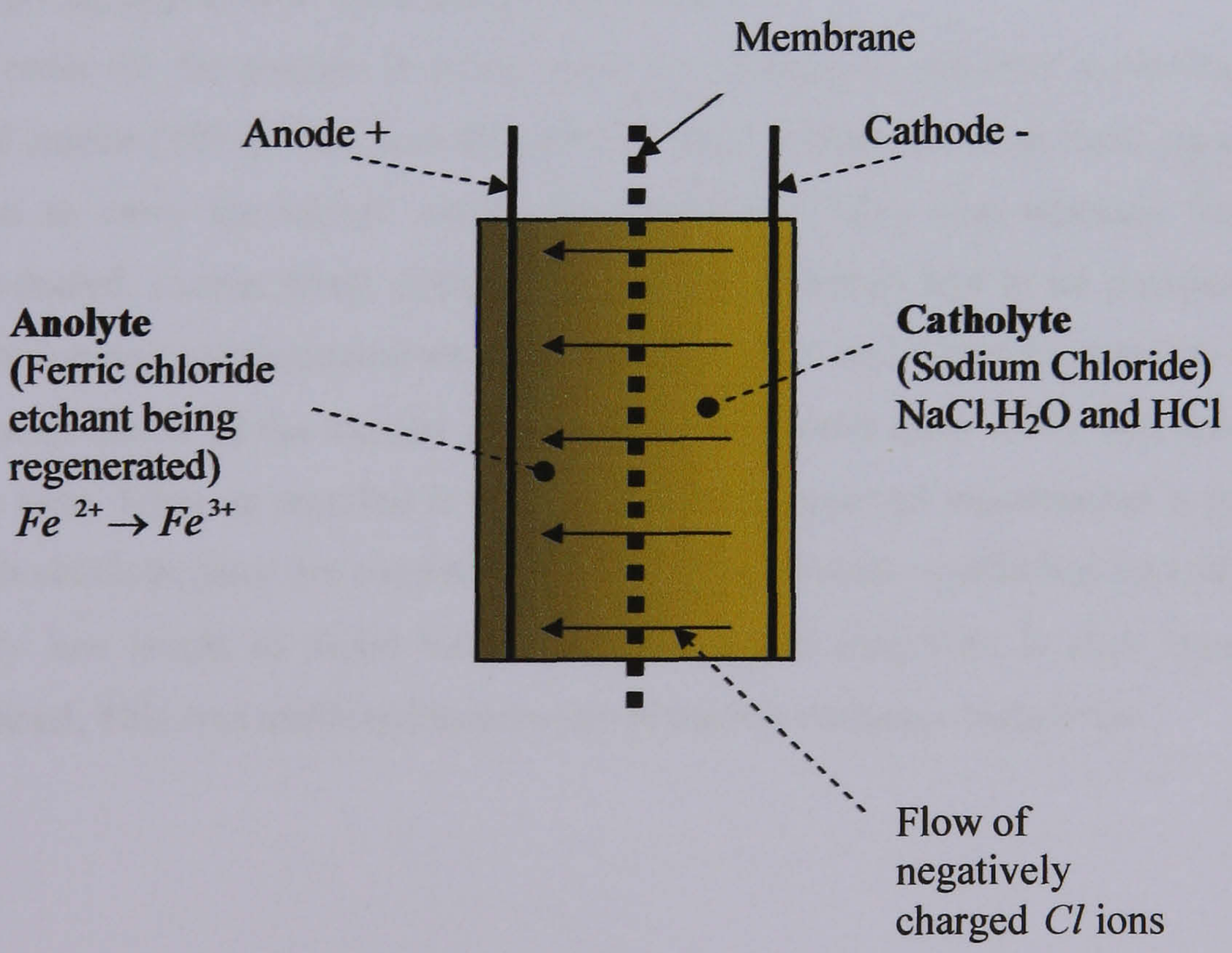


Figure 2.8 Schematic diagram of an electrolytic regeneration cell

Electrolytic regeneration – cont.

A number of different systems has been patented around the world using variations of this generic operation. Some, like the patents granted to Douglas [1968] and Beyer and Lukes [1974] indicated that the process is driven by chlorine gas generation at the anode. Others, like the patent granted to Stehlik [1983], use the diaphragm separation system described above.

In many cases the regeneration system is not continuously connected to the etching machine, but via a series of off-line storage and regeneration tanks. This is said to aid in the removal of sludge [Dorrenbach 1991]. A typical electrolytic regeneration plant is shown in Figures 2.9 and 2.10.

One detailed study of this type of regeneration was carried out in 1992 at Stork Veco, The Netherlands, [Korsse H 1992]. This work indicates that there are some problems with the membranes used, both in the selection of suitable materials and the maintenance of them. Overall the system was shown to be economical and was quoted as giving paybacks in the order of 2 to 3 years.

In order for the process to work, some iron loading is required, according to Visser and Junker [1994]. This is in the order of 33g/l. Below this level there are insufficient ions to carry the charge across the membrane. They also reported that, in tests conducted, excess ferric chloride was produced which had to be pumped off. This solution was contaminated with etchant byproducts and whilst no mention is made of contamination of the etchant in the machine it would seem likely that this would be the case. What is reported is the fact that when constant regeneration is possible the etch characteristics are constant whereas, if the process is switched on and off due to only low levels of metal being dissolved, some variations in etch speed etc. are noticed. This was attributed to porosity of the ion exchange membrane.

Electrolytic regeneration – cont.

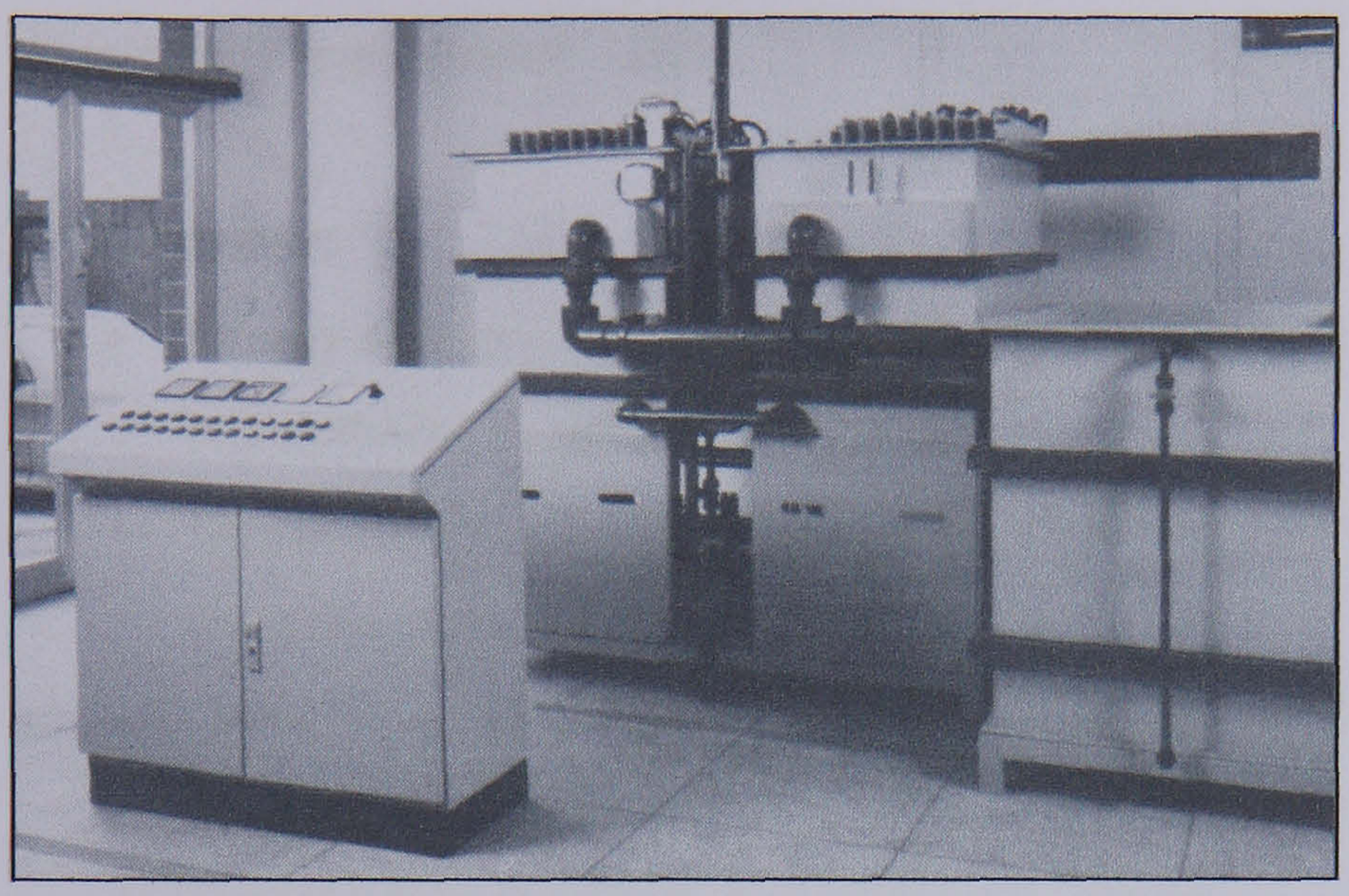


Figure 2.9

Chemapur Electrolytic Regeneration system [Dorrenbach 1991]

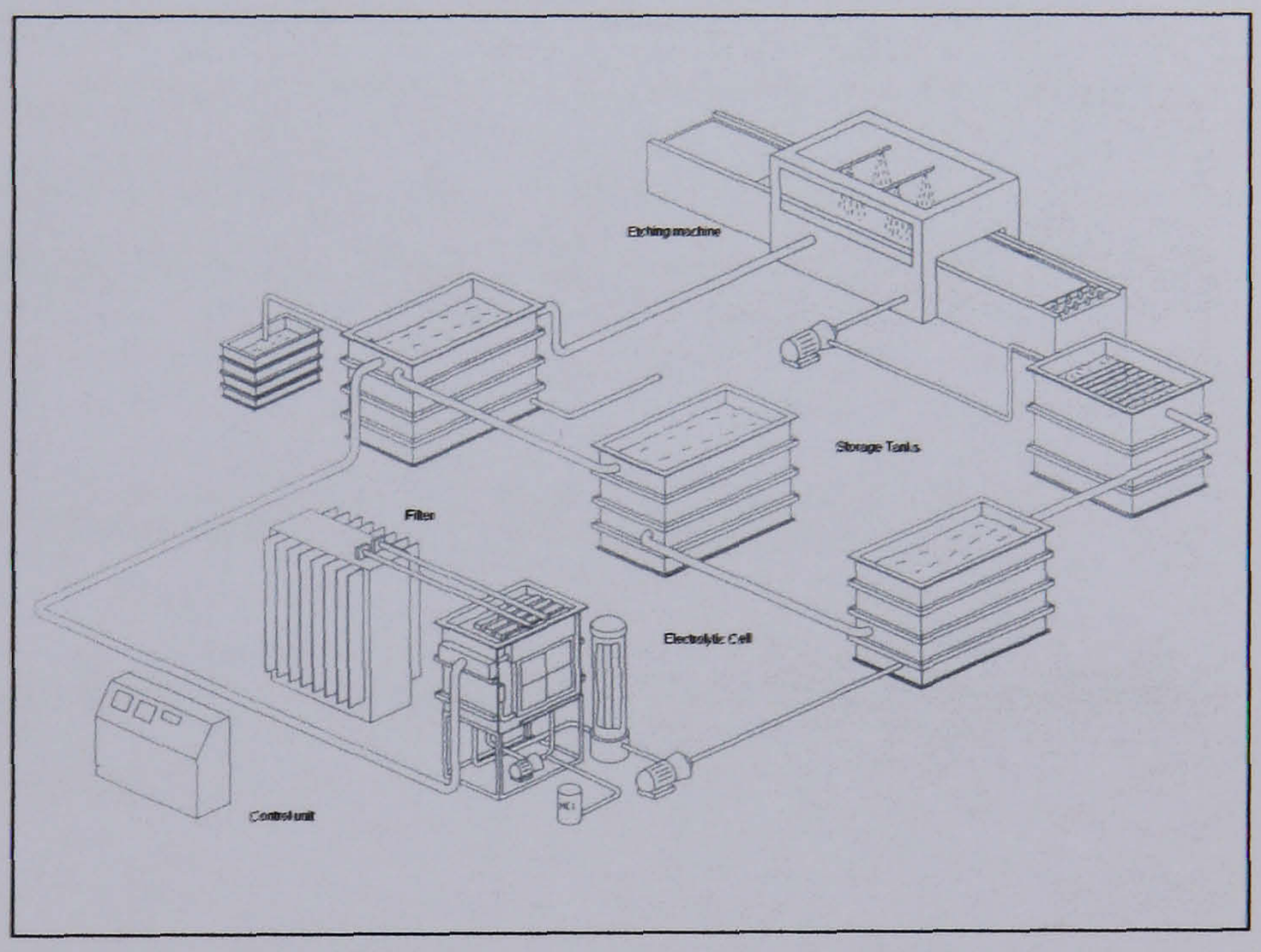


Figure 2.10

Schematic layout of Chemapur system - [Dorrenbach 1991]

Advantages

- No byproducts are present in the solution developed as a result of the regeneration process.
- Dissolved metals, in the form of an iron hydroxide sludge can often be removed from the solution by filtration. Metal is also electrodeposited on the cathode which can be reclaimed.

Electrolytic regeneration – cont.

Disadvantages

- Energy costs are high due to the high currents required to initiate the regeneration reaction within the solution
- Equipment used is more complex than in other systems and requires stringent process control.
- The process generates flammable hydrogen gas which has to be carefully handled to avoid the risk of explosion.
- Only limited commercial equipment is available
- The process uses an exchange membrane which must be maintained in good order to ensure no liquid transfer takes place. These membranes are prone to contamination and rupture which can also stop the reaction.
- The cost of replacement of the membranes can be horrendously expensive.

2.3.3 Sodium chlorate and hydrochloric acid regeneration (BEAC method)

This method of regeneration uses chemical additions to oxidise the ferrous chloride [Robertsons 1987], as shown below :-

$$3FeCl_2 + 3HCl + 1/2NaClO_3 \rightarrow 3FeCl_3 + 1/2NaCl + 3/2H_2O$$

In general, the system senses the ORP of the etching solution and uses this to start addition of hydrochloric acid and sodium chlorate (a strong oxidising agent) when the lower set point is reached. Dosing pumps within the unit add the chemistry to the sump of the etching machine where the reaction takes place. The ORP then rises until the upper set point is reached and the pumps are switched off. Many systems also include a simple probe for monitoring the specific gravity of the etchant and add water automatically. However since a byproduct of the reaction is water, in the tests carried out during this study this was not found necessary. A number of systems for

this type of regeneration are available and a typical design is shown in Figure 2.11. This is a popular system in the USA, Japan and in Europe. Tecan Ltd. has operated such a system for many years and details of tests carried out with this type of system during this study are given in section 5.3.

The first systems were developed by Robertson's Chemicals in the mid 1980's. Many advantages of their uses have been stated including, etchant stability and reduced sludge formation [Robertson 1986]. The system is widely known in the industry by the acronym BEAC which stands for Balanced Etchant Analyser Controller.

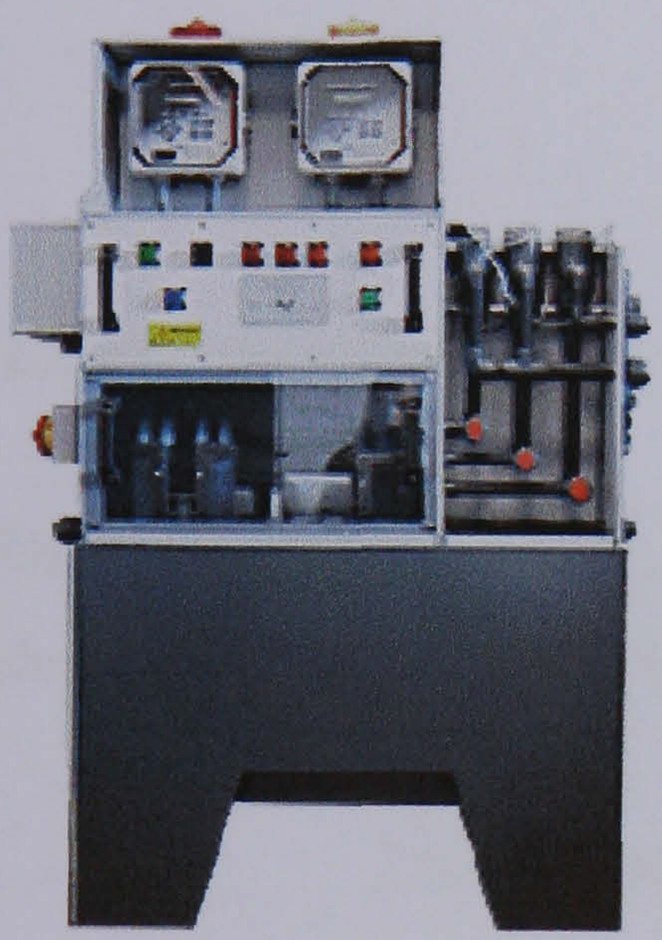


Figure 2.11
A typical sodium chlorate and hydrochloric acid regeneration system, supplied by BLT Circuit Services, (UK). This model is capable of regenerating 8kg of metal per hour.

Advantages

- Comparatively low equipment cost
- Low running cost, both in chemical and electrical requirements.
- Relatively simple chemistry

Disadvantages

- A byproduct of the regeneration is an excess of water which will reduce the SG of the solution and hence affect the etching parameters.
- Sodium chlorate can evaporate and cause a fire hazard when in contact with organic material. Incidents have been reported of farmers' trousers exploding when contaminated with sodium chlorate weedkiller [Pain 2004]
- Build up of hard silicate based scales which can break off and block spray jets causing product rejects.

Disadvantages of BEAC method – cont.

- Equipment can be affected by the fumes from the regeneration process and correct routine maintenance is essential to prevent problems.
- The reaction results in the addition of sodium ions (Na^+) to the etch solution, which will affect the etching parameters.
- If hydrochloric acid and sodium chlorate mix accidentally in the equipment, chlorine gas will be given off. This is extremely hazardous (see section 2.3.1)

2.3.4 Ozone regeneration

Ozone is a strong oxidising agent and it is this property that is exploited to regenerate the ferrous ions (Fe^{2+}) [Allen 1991] in the reaction:-

$$2FeCl_2 + 3HCl + 3/2O_3 \rightarrow 3FeCl_3 + 3/2O_2 + 3/2H_2O$$

Since it is not possible to store ozone, it has to be produced on demand. This is achieved by passing oxygen gas through cold plasma discharge tubes.

An interesting byproduct of the regeneration reaction is the generation of oxygen. This will in itself regenerate, as described in section 2.3.5. No commercially available system is available to PCM companies which is probably due to the hazards associated with ozone and the fact that the gas has to be produced on demand resulting in the need for additional complex equipment and monitoring. A US patent was granted to [Acocella and David (1988)] who claimed that the system could be used to simultaneously rejuvenate acid used in an etching machine, but this work was based mainly on ferricyanide solution used for etching molybdenum.

Advantages of Ozone regeneration

- Theoretically, the reaction is efficient as it has a secondary regeneration due to the very strong oxidisation potential of the ozone. But no data has been found regarding this.

Disadvantages

- Ozone gas is very hazardous: the short term exposure limit (STEL) has been set at 0.3ppm [Occupational Exposure Limits 2002 EH20]
- The gas is explosive in concentrations higher than 20% by volume. Therefore ozone cannot be stored and has to be generated at the time of use.
- No commercial equipment is available for this process..
- A byproduct of the reaction is water which will dilute the etch solution and affect the etching parameters.

2.3.5 Oxygen regeneration

The regeneration of the ferrous chloride to ferric chloride with oxygen is determined in this system by the formula

$$4FeCl_2 + 4HCl + O_2 \rightarrow 4FeCl_3 + 2H_2O$$

The process has the obvious advantage that no specifically dangerous chemistry is used and no harmful byproducts are present in the regenerated solution.

No commercial equipment is available for the exploitation of the process. A patent was granted to IBM [Lubert 1993] but this was used solely as an in-house process. Some research was undertaken at Cranfield in 1993[Ler 1993]. In 1997 IBM released the patent to the Photo Chemical Machining Institute (PCMI) and further research was undertaken at this time [Ler 1998]

The fact that air contains 21% oxygen also presents the interesting possibility that air could be used to regenerate the solution. A number of PCMI members have spoken

about extended etchant life times being achieved by leaving etching machines running overnight. It would seem likely that they have unwittingly used this reaction without fully understanding how the extended life of the solution has been achieved.

As will be shown in chapter 7 this does appear to be a realistic possibility and nothing could be considered more environment friendly than the use of air.

2.4 Previous Oxygen regeneration research

Initial research was undertaken using a laboratory experimental set-up [Ler 1993]. In these tests, oxygen was bubbled through a small volume of ferrous solution. The results showed that oxygen could be used to regenerate spent ferric solution but that the reaction rate was slow. Varying the concentration of hydrochloric acid concentration had little effect but increasing the flow rate of oxygen improved the reaction rate.

As part of a wider study on the environmental effect of photoetching, this research was continued at Cranfield in 1995 [Ler 1998]. During this study a production etching machine was modified to allow the dosing of oxygen and hydrochloric acid. A number of tests was carried out which again showed that the system was capable of regeneration, albeit at a slow rate. The conclusion was that the system could be cost-effective for companies who only etched small volumes of metal. It was clear that, to become a viable commercial system, some form of automation would be required.

Further work was undertaken on production equipment [Peter 1999]. This study concentrated mainly on the development of a sophisticated automated system for monitoring the etch solution and initiating the oxygen dosing. The results of the regeneration again looked encouraging with the ORP showing marked increases when the system was running. However both this and the previous tests were only conducted over a very limited time period and the regeneration tests, on average, only lasted a few hours. In this work Peter reported very low regeneration efficiencies, stating that they were only around 3%. It was felt that in order to investigate the full

potential of the oxygen regeneration and develop more efficient systems long term production tests were required. It is against this background that this study was undertaken.

2.5 Survey of industrial trends

The results of a previous industrial survey are summarised in Figure 2.12 and 2.13 [Allen and Ler 1999]. From these figures it can be seen that 44% of the companies responding did not regenerate. The main reasons for this were stated as being lack of technical knowledge and the fact that companies did not feel regeneration would contribute to the company's profits. The latter is a little surprising considering that even basic calculations show this not to be true, unless companies are using very small volumes of fresh solution. However, no record of the volumes being etched was available. Other factors given for not regenerating were lack of space, low usage of ferric chloride and health and safety considerations, particularly in relation to chlorine. From the survey it was also apparent that companies would be prepared to invest in regeneration systems that were more environment-friendly. This would of course be true for a system using oxygen.

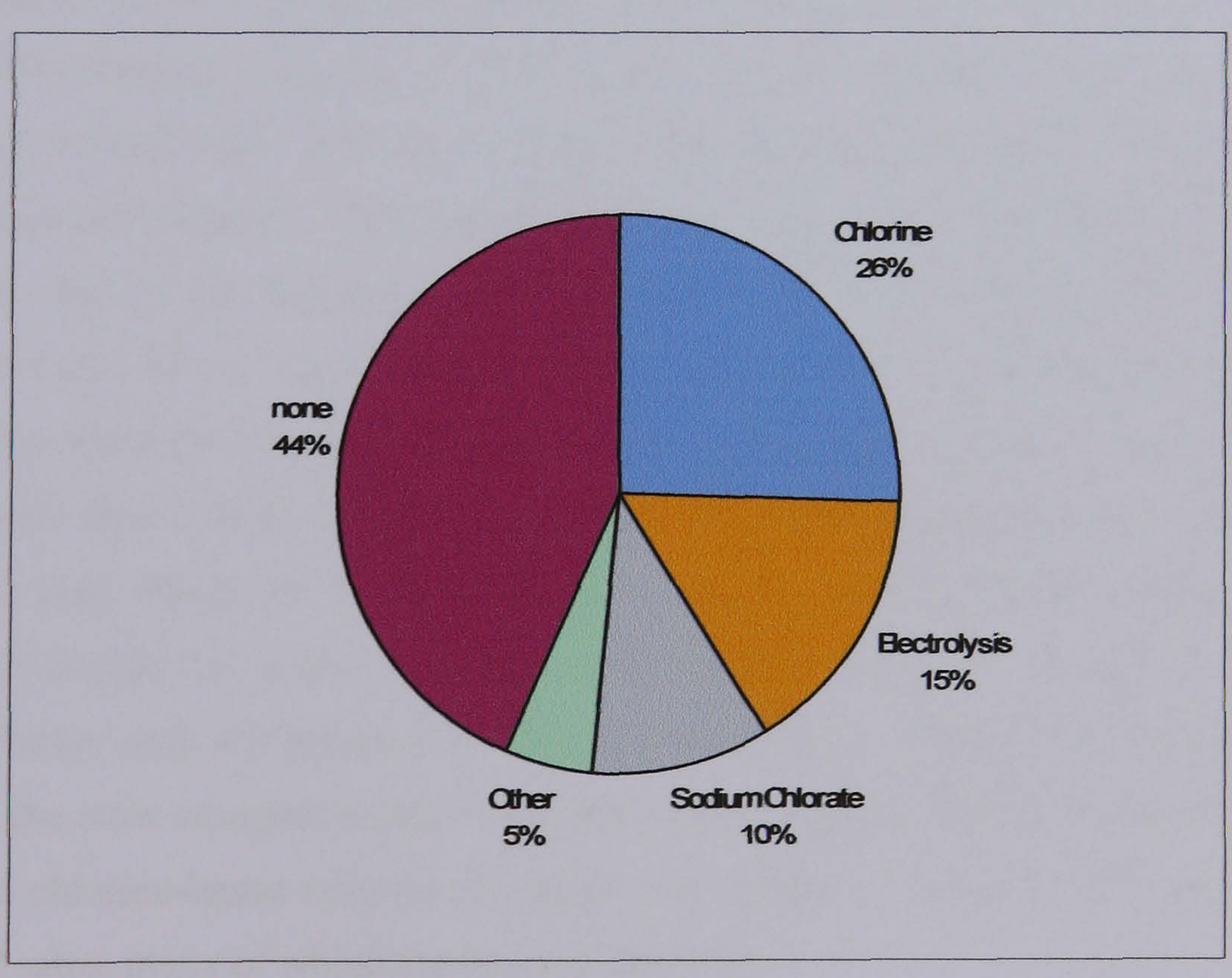


Figure 2.12 Summary results of regeneration methods. Survey conducted in 1998. [Allen and Ler 1999].

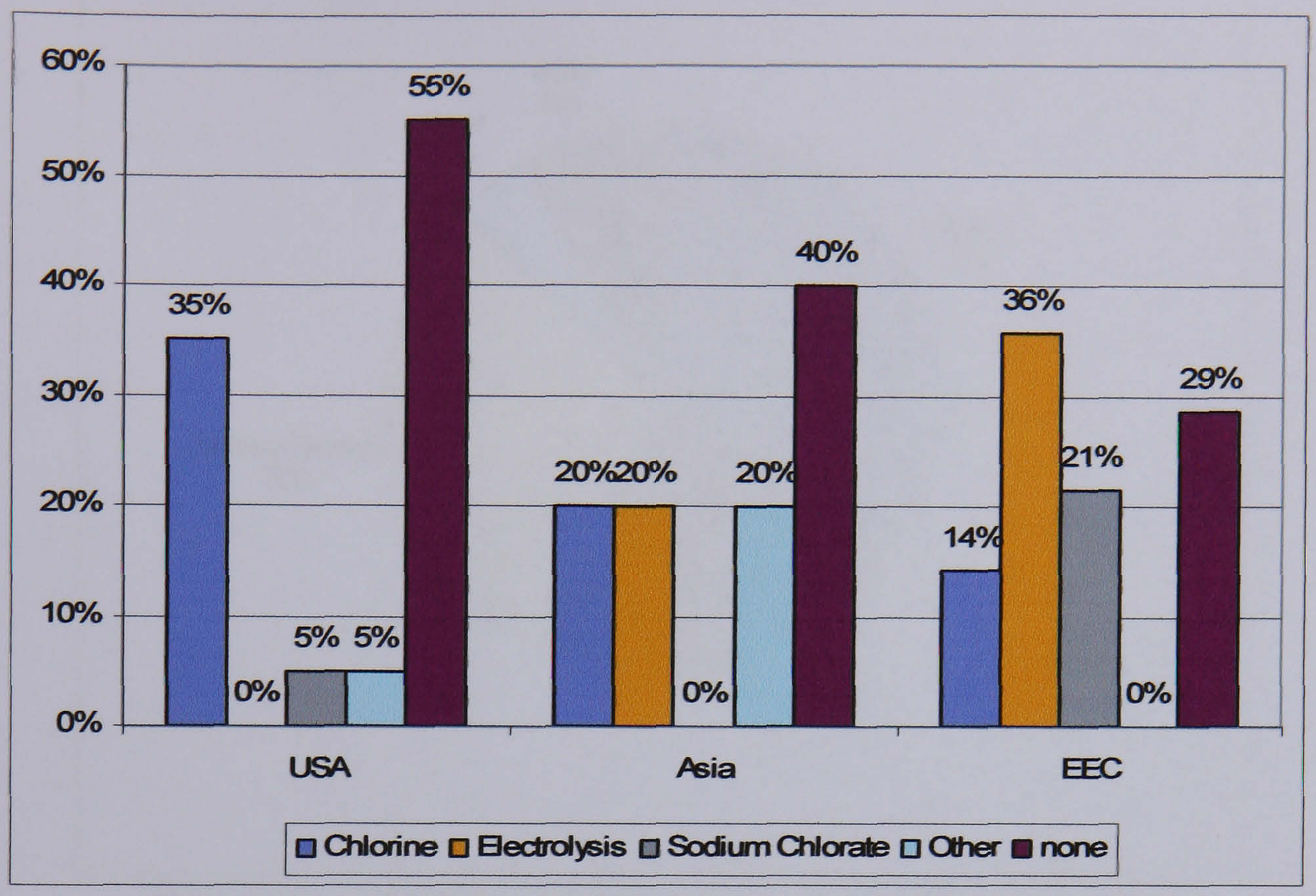


Figure 2.13 Summary results of regeneration methods by area. [Allen and Ler 1999].

A further survey was carried out (as part of this study) in 2004 amongst members of the PCMI attending a conference in Glasgow. The results of this survey are given in Figures 2.14 and 2.15 . The most striking difference between the two surveys is the percentage of companies regenerating. This had risen to over 90% and this is almost certainly due to the increasing costs of both fresh ferric chloride and increased disposal costs of the spent solution. This, coupled with increasing environmental issues, has forced more and more companies to install regeneration systems. The 2004 survey still shows marked differences between the USA and Europe in terms of the methods used. Plants in the USA predominately use chlorine-based systems (67%), whilst in Europe the sodium chlorate and electrolysis methods are equally popular, with chlorine only representing 14% of the total. This is probably due to two major factors: the more stringent legislation controlling the use of chlorine in Europe and the fact that chlorine-based systems are more cost effective in plants with higher metal removal rates, many of which are based in the USA.

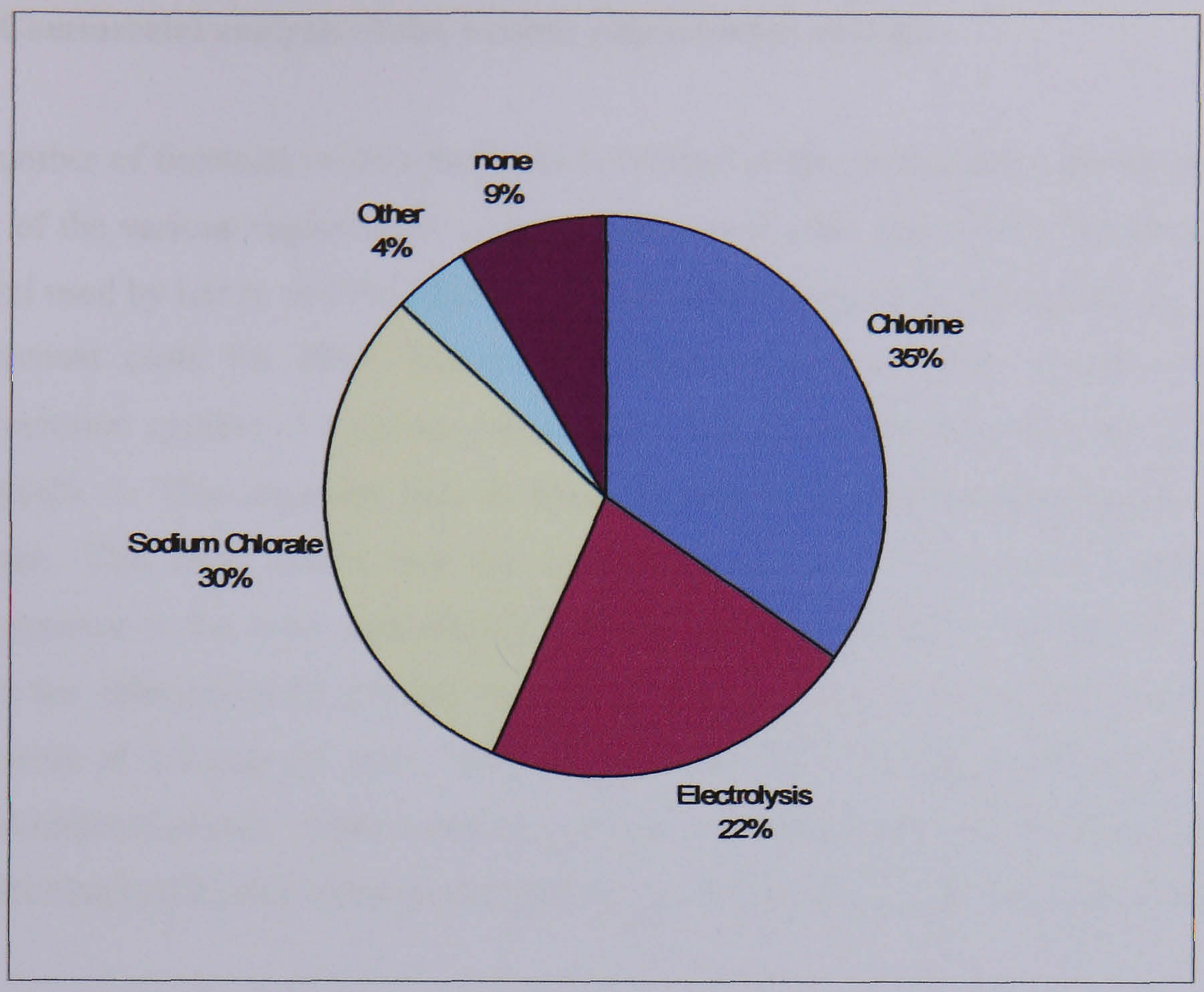


Figure 2.14 Summary results of usage survey conducted in 2004

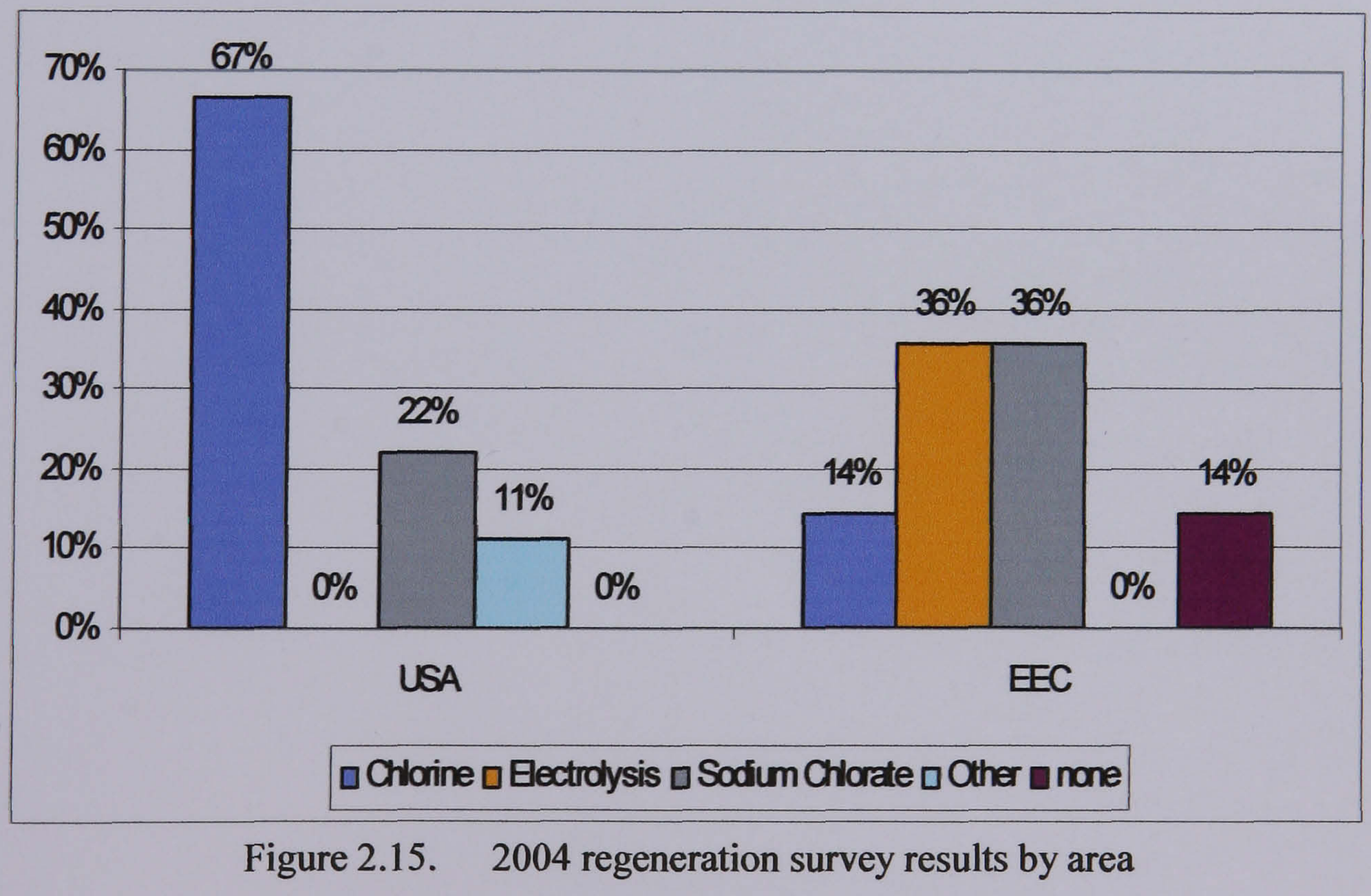


Figure 2.15. 2004 regeneration survey results by area

2.6 Commercial analysis of the various regeneration systems

A number of financial models has been developed in the past to show the theoretical cost of the various regeneration systems [Allen et al 1991 and 1992]. The economic model used by Ler in this PhD thesis [1998] has been updated to current chemical and equipment costs for 2005. Figure 2.16 shows a plot of costs for the various regeneration systems, the update calculations used to compile this chart are given in Appendix 3. This appendix also includes theoretical figures for regeneration with oxygen. This chart shows that the sodium chlorate and hydrochloric method of regeneration is the most cost effective system for low volumes of processed metal, while the chlorine-based systems become more cost-effective when etching volumes in excess of 1 tonne per year. This would account for chlorines popularity in high metal removal plants. Some comparisons between these theoretical figure and actual results obtained by this research and general investigations are given in chapters 6 and 7.

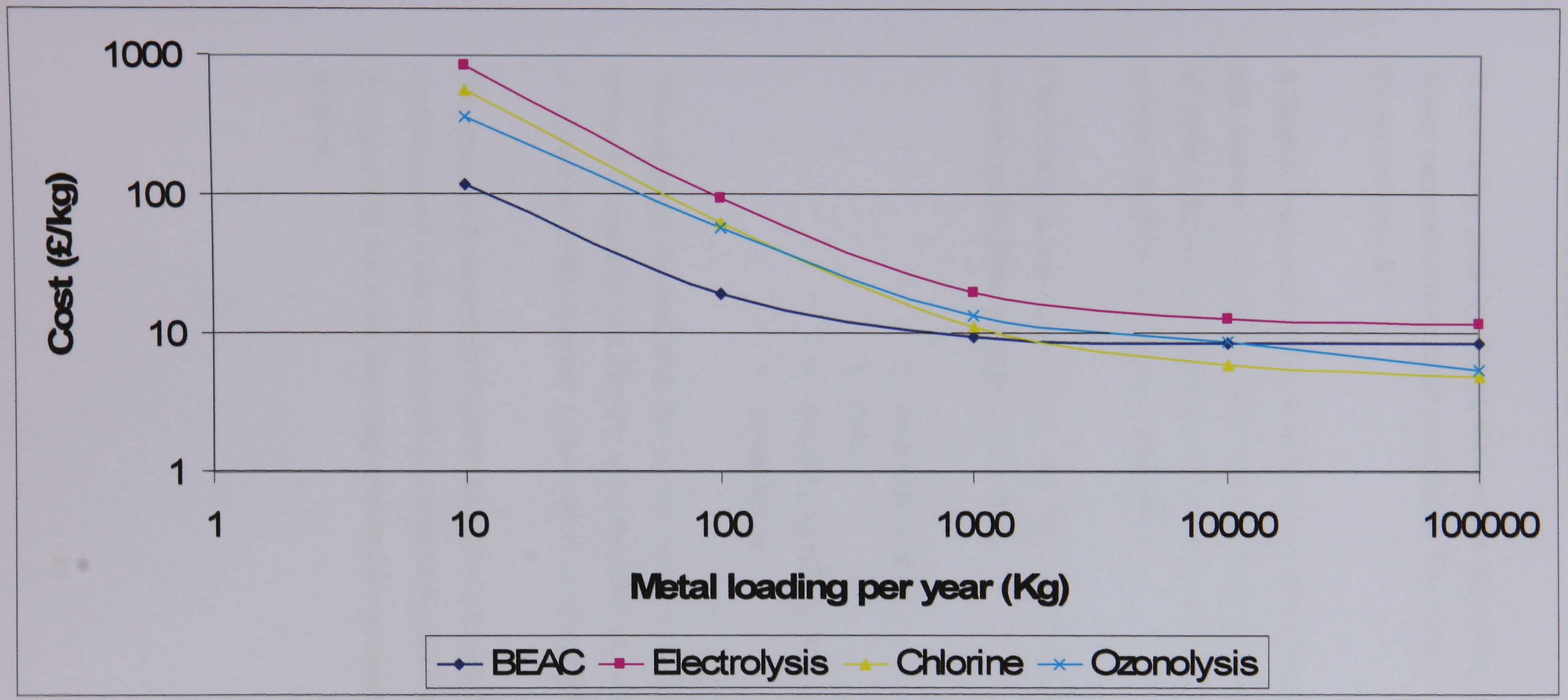


Figure 2.16 Regeneration costs for various methods and metal loading rates.

3 Control Parameters

3.1 Introduction to control measures

In producing parts by the photochemical machining process a large number of inter-related parameters have to be considered. These can be divided into four main groups as shown in Figure 3.1.

A large amount of previous research has covered many aspects of the material selection and machine set-up [Visser and Weissinger 1993]. To consider the interrelated effects of all of these parameters would not have been possible in this study, so only those related to etchant chemistry have been considered.

Chemically it has been shown that the key chemical parameters which need to be considered are [Almond and Allen 2004].

- Free acid content
- ORP
- Baumé (specific gravity)
- Temperature

This research showed that due to the complex interrelations of the parameters listed above, it is essential that they are not considered as individual measurements but are used as a guide to 'build a picture' of the condition of the etchant.

The research discussed by Almond and Allen is largely based on work undertaken in lab conditions and whilst some work has been published in industrial-based situations [Korsse 1993] this is the first long-term and comprehensive study of these measurement systems.

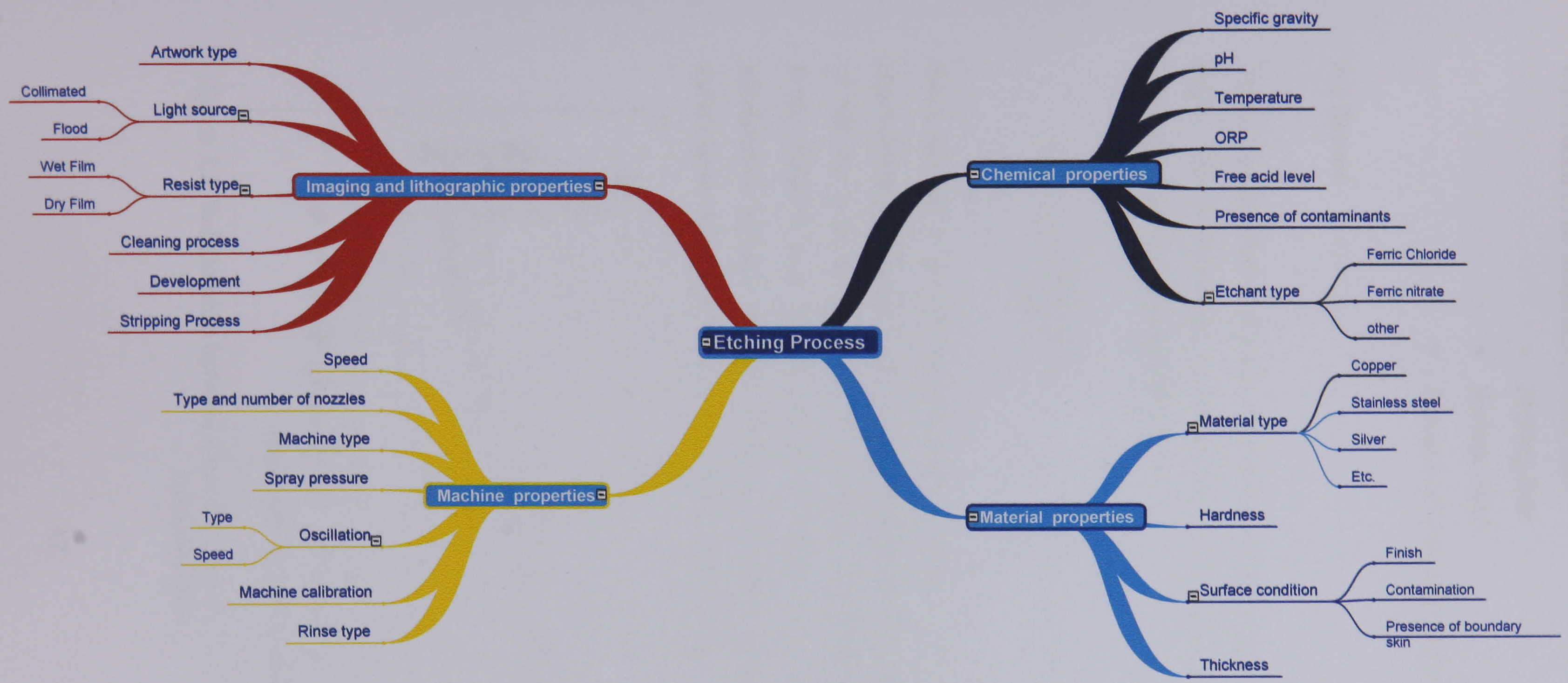


Figure 3.1 Key factors which affect the etching process

In order to determine the overall efficiency of the process, there are other key indicators which need to be monitored. These are:-

- Etching Rate
- Surface finish
- Amount of material dissolved into solution

3.2 Baumé

Typically the dilution of ferric chloride etching solutions is measured on the Baumé (°Bé) scale. This is calculated by measuring the specific gravity of the solution and then substituting in the following formula:

$$°Bé = 145\frac{(SG-1)}{SG} \qquad \text{where SG = the Specific Gravity}$$

Since the SG is directly related to the molarity of the unused solution this is a good measurement of the chemical strength of the solution, indicating that the higher the value of °Bé the more concentrated the solution. The relationship between concentrations of ferric chloride and °Bé is shown in Figure 3.2. An extensive table showing the relationship between SG, °Bé, Molarity and other concentration indicators together with the formulae that relate to them is given in Appendix 4.

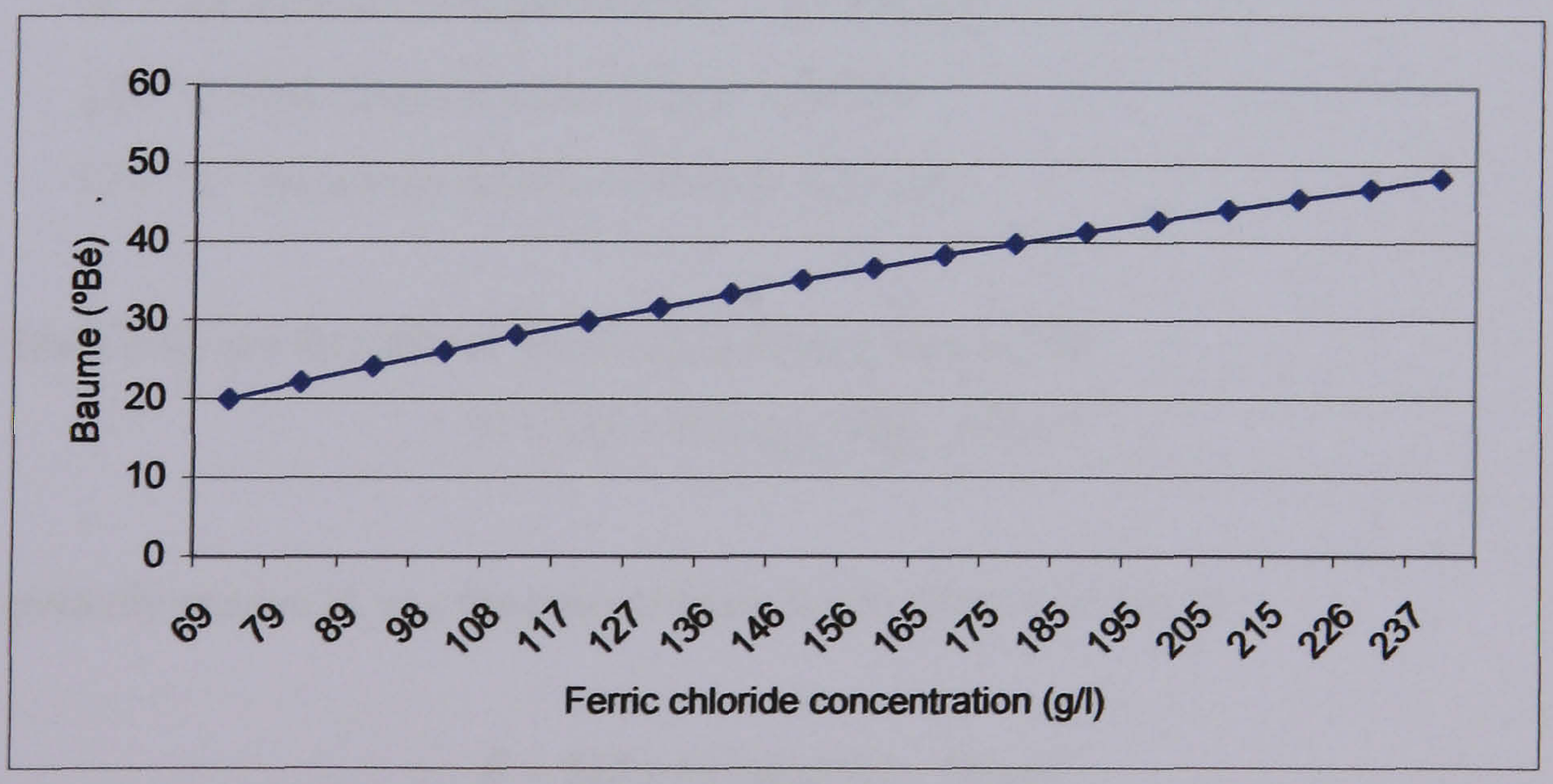


Figure 3.2 Relationship between Baumé (°Bé) and Ferric chloride concentration [Allen, Almond 2004]

The usual range for commercial etchant is between 36 and 42 °Bé. Lower values will increase the etch rate but can lead to poor surface finish [Allen and Herarty 1980 and Beaupre 1987]. Etching solutions as low as 20 °Bé have, however, been used in the sponsoring company to etch aluminum alloys where a low concentration of ferric is all that is required to dissolve this low corrosion resistant material.

3. 3 Oxidation reduction potential (ORP)

As metal removal takes place in the etching process the ratio of ferrous ions Fe^{2+} to ferric ions Fe^{3+} (the active element) will increase. ORP can be defined mathematically by the Nernst equation.

$$E = E^{o}_{formal} + \frac{2.303RT}{nF} \times \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Where,

E =ORP (V)

E^{0}_{formal} = electrode potential of the concentrated solution (V) (in our case 523 mV)

R = the gas constant (8.31 J/mol K)

T = the absolute temperature (K)

n = the number of electrons changes in the Redox reaction

F = the Faraday constant (9.6485×10^{4} C/mol)

$[Fe^{3+}]$ = the concentration of ferric ions (M)

$[Fe^{2+}]$ = the concentration of ferrous ions (M)

For fresh acid, say the ratio of ferric ion to ferrous ions is 100

$$E = 523 + 60\log_{10}[100] = 643mV$$

For partially-used acid, say the ratio of ferric ion to ferrous ions is 10

$$E = 523 + 60\log_{10}[10] = 583mV$$

From the Nernst equation it can be seen that as the ratio of ferric to ferrous changes the ORP will change. ORP can therefore be considered as an indicator of the activity level of the etchant.

However, other parameters will affect the ORP. Figure 3.3 shows how the ORP increases as the temperature and/activity of the etchant changes. The free acid content of the etchant will also affect the result. Increasing levels of free acid will reduce the ORP values.

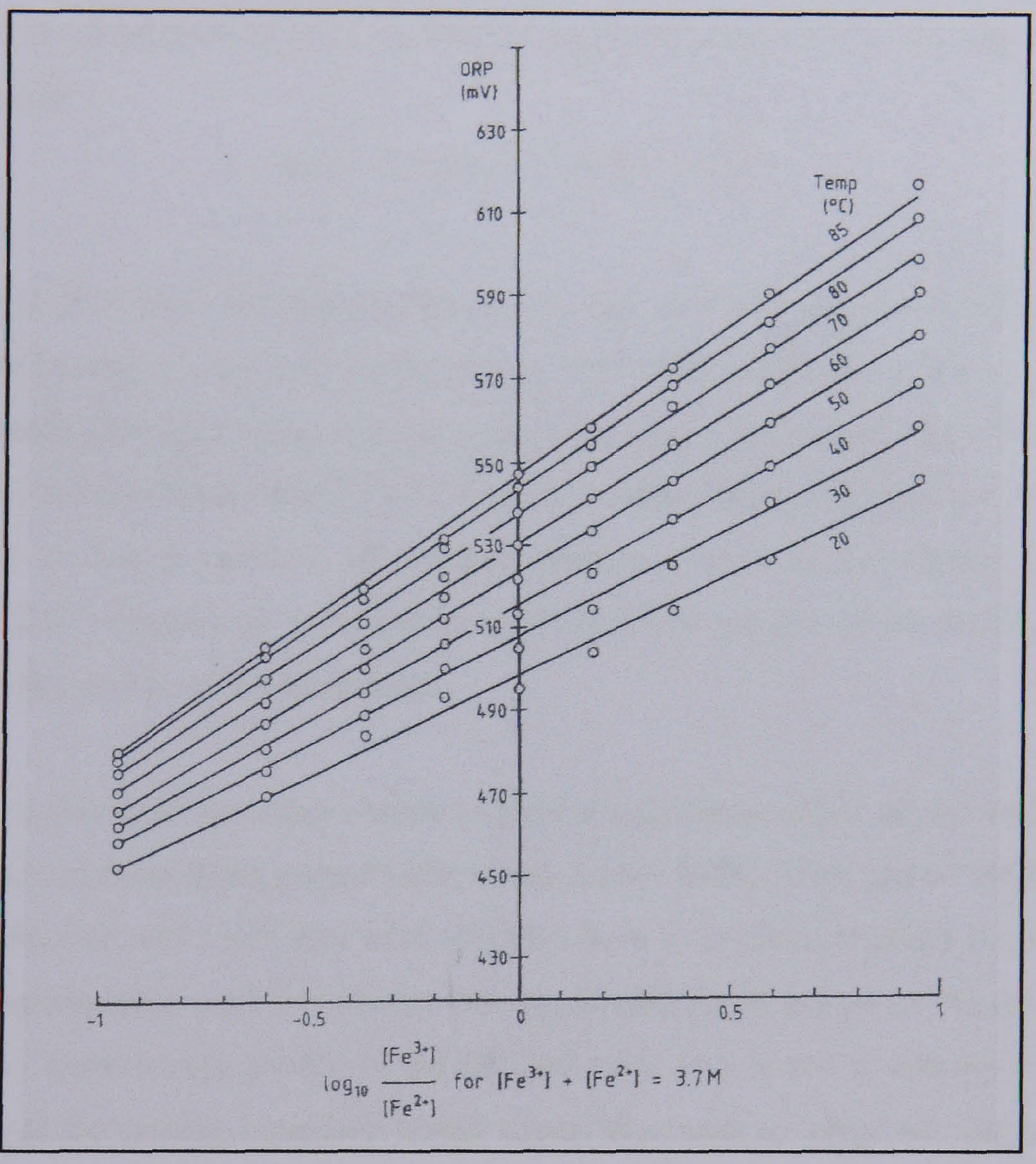


Figure 3.3 ORP verses Temp [Allen, Almond 2001]

Typically, the value of the ORP is used to trigger the regeneration process. Monitoring equipment detects the falling ORP, switches on whatever system is installed, this regenerates the etchant, the ORP raises until an upper set point is reached at which point

the regeneration is turned off. As will be seen later, the value of ORP cannot be considered in isolation to other parameters. The free acid level and amount of dissolved metal in solution affect the actual reading and therefore must be taken into account.

3.4 Free Acid

Hydrochloric acid (HCl) is present in the etching solution and is often referred to as 'free acid'. Hydrolysis of ferric chloride will occur naturally when mixed with water according to the formula:

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_3 + 3HCl$$

Additions of HCl will shift this reaction to the left and help to prevent this hydrolysis which would result in the precipitation of the metal. The HCl acts as a source of chlorine to allow metal chlorides to be formed rather than metal hydroxides, thus the additions increase the metal holding capacity of the solution. When the free acid is low it would not be unusual to see a build-up of metal-containing sludge in the bottom of etching machines. This is extremely undesirable as it will block the jets of the etching machine and reduce the quality of the final parts.

The level of free acid has been shown to have a significant effect on the etch rate and surface finish of parts being etched [Visser and Junker 1994, Allen and Li 1988, Beaupre 1987]. In practice, too much free acid will also have a detrimental effect on the etching process. Experimental work has shown that concentrations in excess of 3% (by vol.) can cause a very uneven edge profile of the finished part. This is due to delamination of the photoresist at the etching boundary which causes the resist to 'chip' off and expose the surface of the metal which will then be attacked by the acid. Typical etch profiles are shown in Figure 3.4. The part shown on the right clearly shows a breakdown around the edge due to the free acid level being too high.

As HCl is a gas and the etching process is carried out at elevated temperatures some HCl will evaporate. This will cause the reaction shown above to move to the right, resulting in further hydrolysis.

Therefore monitoring of the free acid level is clearly essential for control of the process.

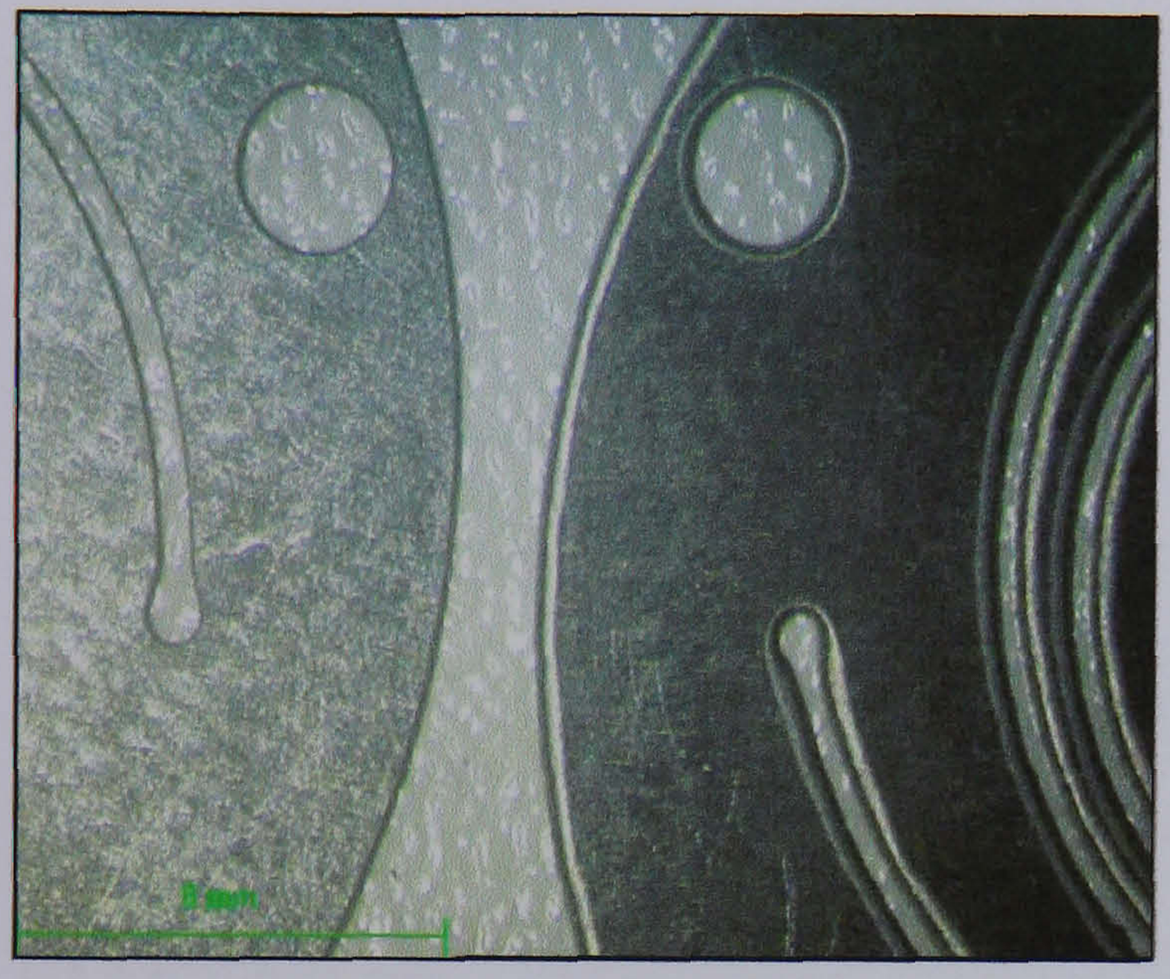


Figure 3.4

Breakdown due to excess free acid – part on the right was etched with 1.7% free acid and shows typical delaminating effects around the etch boundary, part on the left was etched with 0.3% free acid and shows a far superior edge profile.

Historically, titration has been used to determine the free acid level. Numerous methods of determining the free acid by titration have been developed [Allen and Almond 2004, Scarpellino 1996]. Appendix 5 shows a selection of the titration methods typically used in industry. However, the accuracy of this type of analysis has been shown to be in doubt due to the complexes which will exist in the etching solution once etching has started and metal ions are present. It is also very susceptible to operator error since it relies on the operator determining the end point for some reaction during the titration process. Titration methods are also very time-consuming, making them wholly unsuitable for in-process measurement.

Tecan used the titration procedure known as the *'Interconics method'*. This is based on complexing with sodium thiosulphate and pH monitoring. The full method is described in Appendix 5.

Using the direct measurement of pH as a convenient method of monitoring free acid was suggested by Allen[1988]. A further method using conductivity has also been discussed [Almond and Allen 2005].

3.4.1 Measurement of pH as a means of determining free acid

pH is a measure of the concentration of hydrogen ions (H^+) according to the formula:

$$pH = -\log_{10}[H^+]$$

Hence a low pH will indicate a high free acid level. The strongly acidic ferric chloride etching solutions produce negative pH numbers and whilst some debate exists regarding the absolute meaning of negative pH values [Muwanga-zake 2002 and Senese 2005]. It was felt that, as will be seen below, there was a sufficiently sound relationship between pH and the actual free acid level obtained by adding exact amount of HCl to the etchant, to make this a very suitable measurement method.

Typical results from the research carried out are given in Figure 3.5 [Allen and Almond 2004]. These results were undertaken on a lab scale and it was felt desirable to confirm these in the industrial setting. The results of these tests are given in Figure 3.6 and confirm the previous research. The variations seen can probably be attributed to temperature effects and variations in the set up and calibration of the two systems.

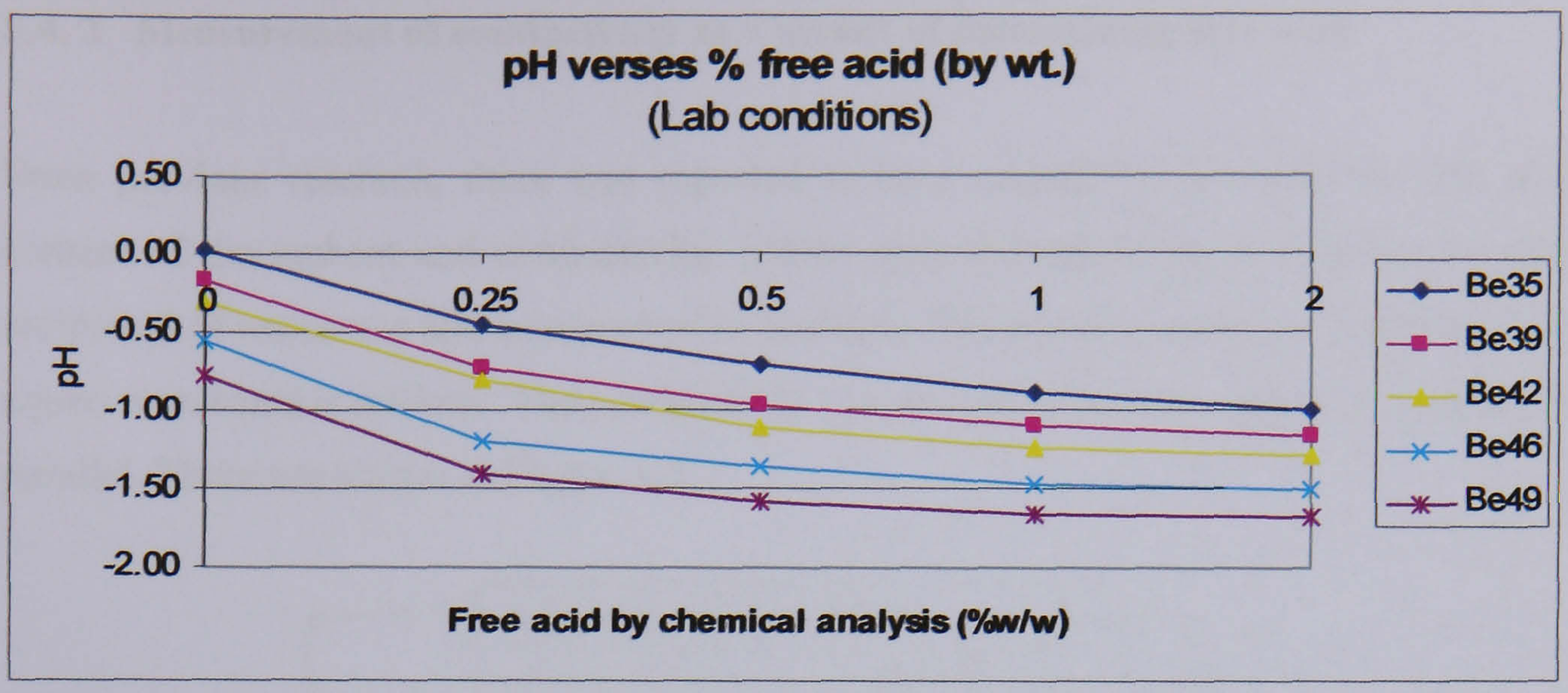


Figure 3.5 pH versus free acid for various concentration of virgin ferric solution.

(These results were taken from previous research carried out under lab conditions)

[Allen and Almond 2004]

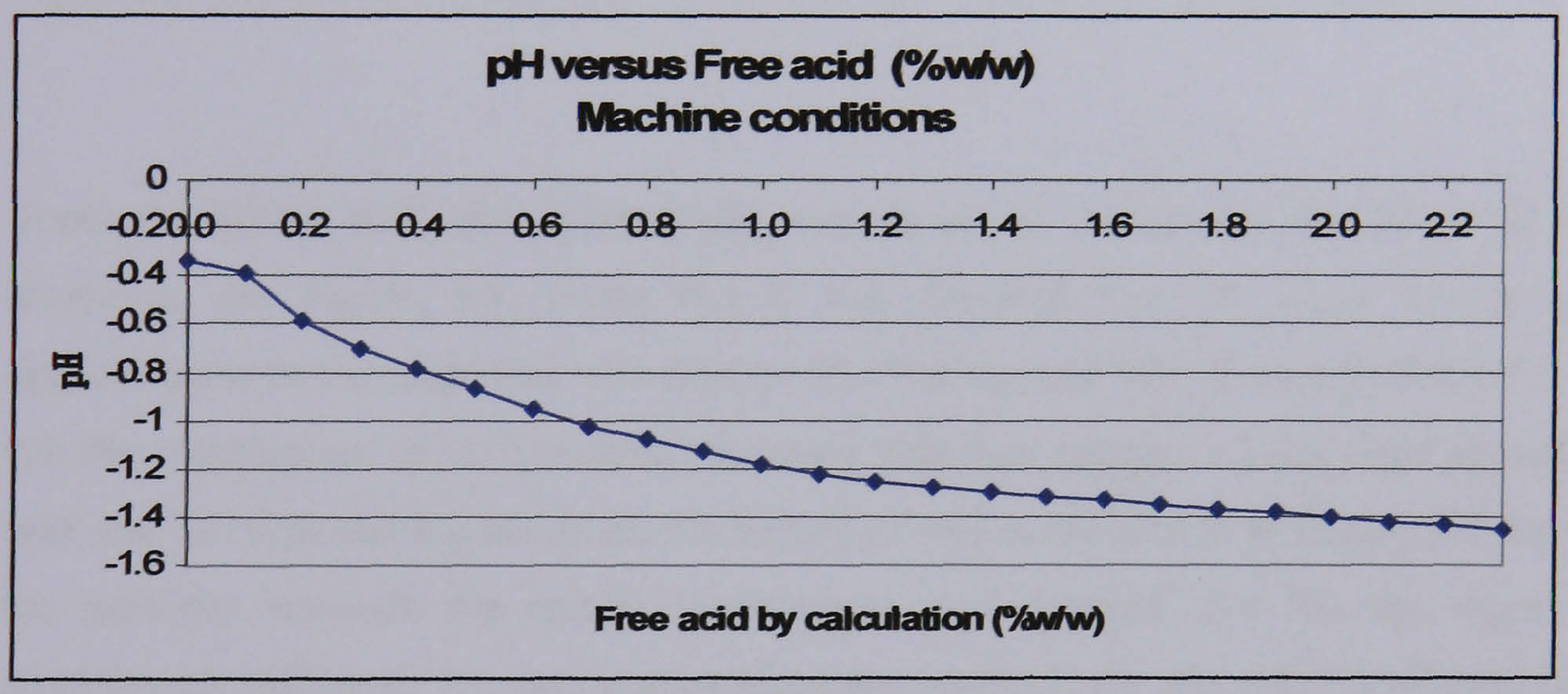


Figure 3.6 pH versus free acid for 39 °Bé ferric solution under machine operating conditions

As the ferric chloride etchant is such a strongly acidic solution it would destroy conventional lab type pH probes and hence they are wholly unsuitable. However a pressurised pH probe of the type detailed in Appendix 6 will last for a considerable length of time. One was used continuously in this study for 16 months.

3.4. 2 Measurement of conductivity as a means of determining free acid

From previous research, there was reported to be a correlation between the free acid content of the etchant and conductivity, [Allen and Almond 2004]. Conductance is the reciprocal of resistance and is measured in Siemens. The usual measure of conductivity in aqueous etchants is mS/cm. The conductivity is made up of four key elements working in parallel. These are shown in Figure 3.7.

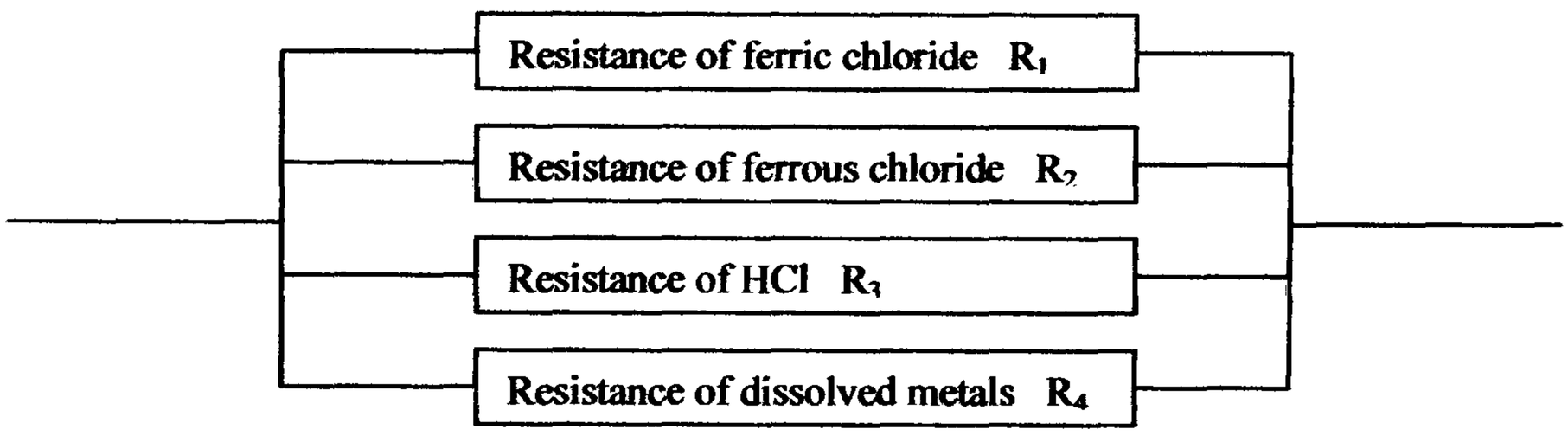


Figure 3.7 Resistances of the various elements in the etchant working in parallel

From the above study the conductivity was shown to increase as the free acid level increases, see Figure 3.8. From this it was deduced that the slope of the chart approximates to a straight line with a slope of 15mS/cm per %HCl. As with the pH it was felt that verification of the previous lab-based tests was required. Tests were carried out with the full size etching machine, the results of which are shown in Figure 3.9 As with the previous research the results approximate to a straight line but the slope was significantly different. No easy explanations are available for this but it is thought likely that differences in the equipment configuration and calibration could be responsible. What is certain from the work undertaken during this study is that the results with the equipment used are repeatable for similar acid conditions.

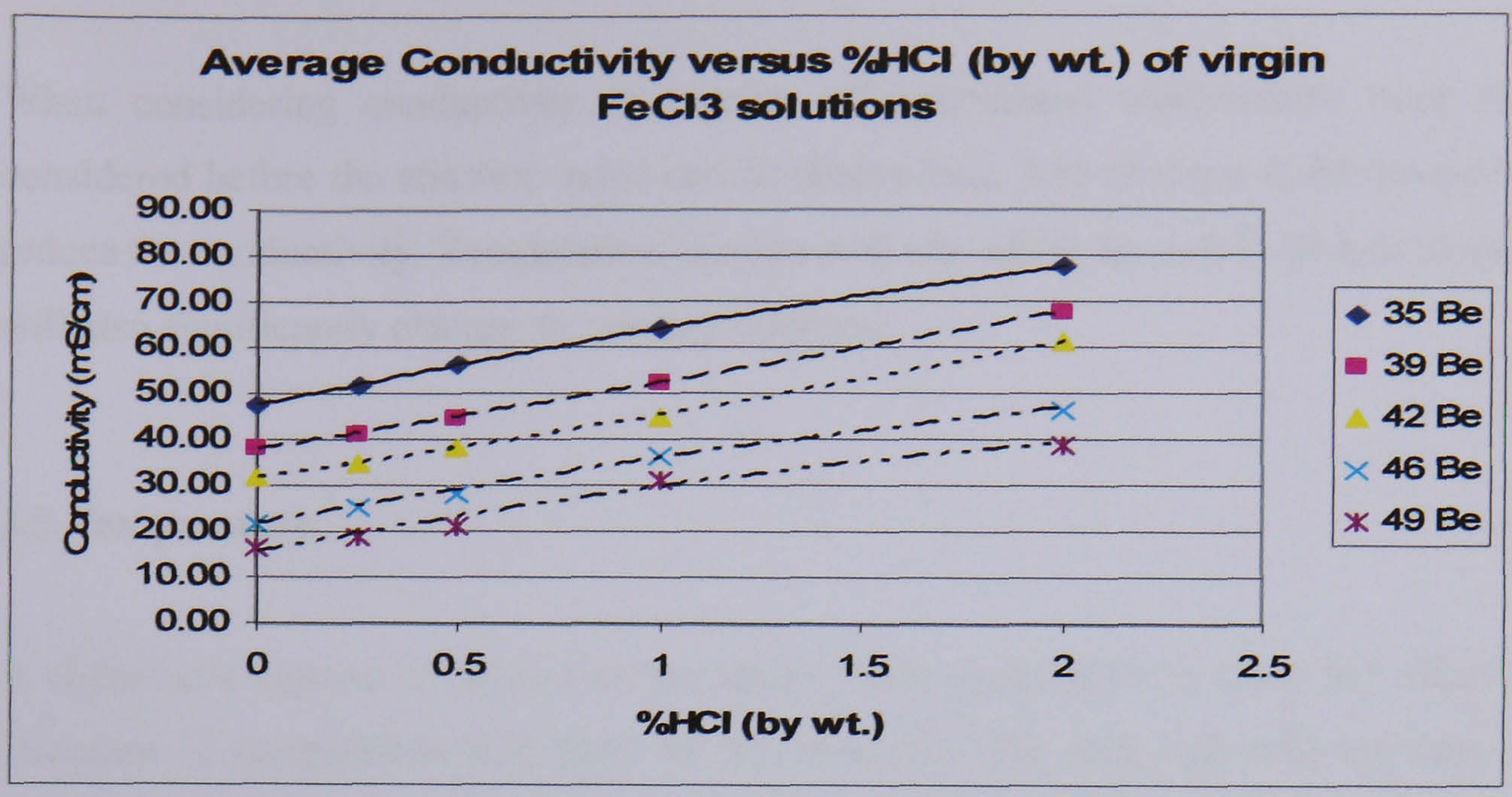


Figure 3.8 Conductivity versus Free Acid (lab test) [Allen and Almond 2004]

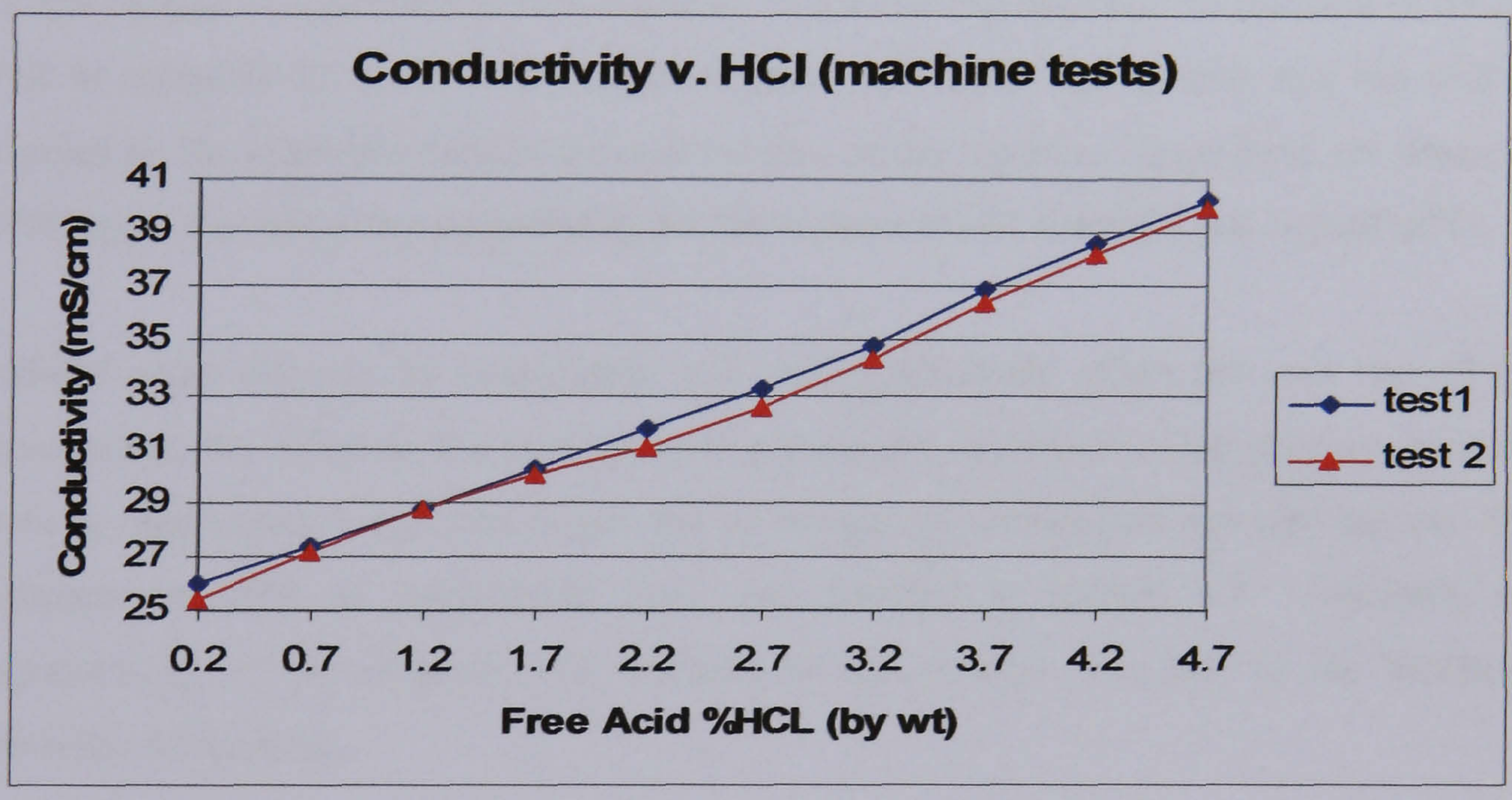


Figure 3.9 Conductivity versus Free Acid

(Machine test carried out at Tecan with ferric etching solution of 38 °Bé)

The main reason to consider conductivity as a means of determining free acid levels is the relative ease of the measurement method. Both the monitoring equipment and probes are in common use in other chemical measurement areas and are built to a standard that will survive in the harsh environment around commercial etching plants. Full details of the equipment used are given in Appendix 7.

When considering conductivity, a number of interrelated relationships need to be considered before the absolute value can be determined. Any increase in the Baumé will reduce the conductivity. Temperature changes will also affect the result. Dissolved metals will also significantly change the reading obtained.

3.5 Temperature

A significant amount of work has previously been undertaken to show the effect that increases in temperature will have on the etch rate. The etch rate will increase with increases in temperature due to the increased mobility of the ions and the ability of the etchant to hold dissolved metals, [Allen 1986]. In a commercial operation the temperature of the etchant is controlled thermostatically in the etching machine. In the case of Tecan, this is normally 52°C. Increases in temperature will speed up the etch rate but will be limited by the materials used in the construction of the machine. Since these are normally PVC-type, the maximum temperature for the etchant would normally not exceed 60°C.

Whilst small changes in temperature will not significantly affect the etch rate of the production, the effect in the measurement parameters described in the previous sections will be significant. Variations of pH due to changes in temperature are well known. The increase in ORP as temperature rises was detailed in section 3.3. Similarly the conductivity of the solution will increase as temperature rises due to the increased mobility of the ions.

The SG of the solution will fall as temperature increases due to the increased volume. Hence, the Baumé of the solution will also fall as temperature increases.

In this study, the temperature was kept as constant as the etching machine control system would allow. A typical profile of a day's results is shown in Figure 3.10. From this it can be seen that the variation is only +/- 0.45°C. The small changes seen can be attributed in the main to the delays in response time of the control system. No appreciable changes are seen as a result of loading the machine with parts. It was not considered that the level of

variation seen would have had any significant affect on the results of this research. ORP also affects the conductivity, this is shown in Appendix 9.

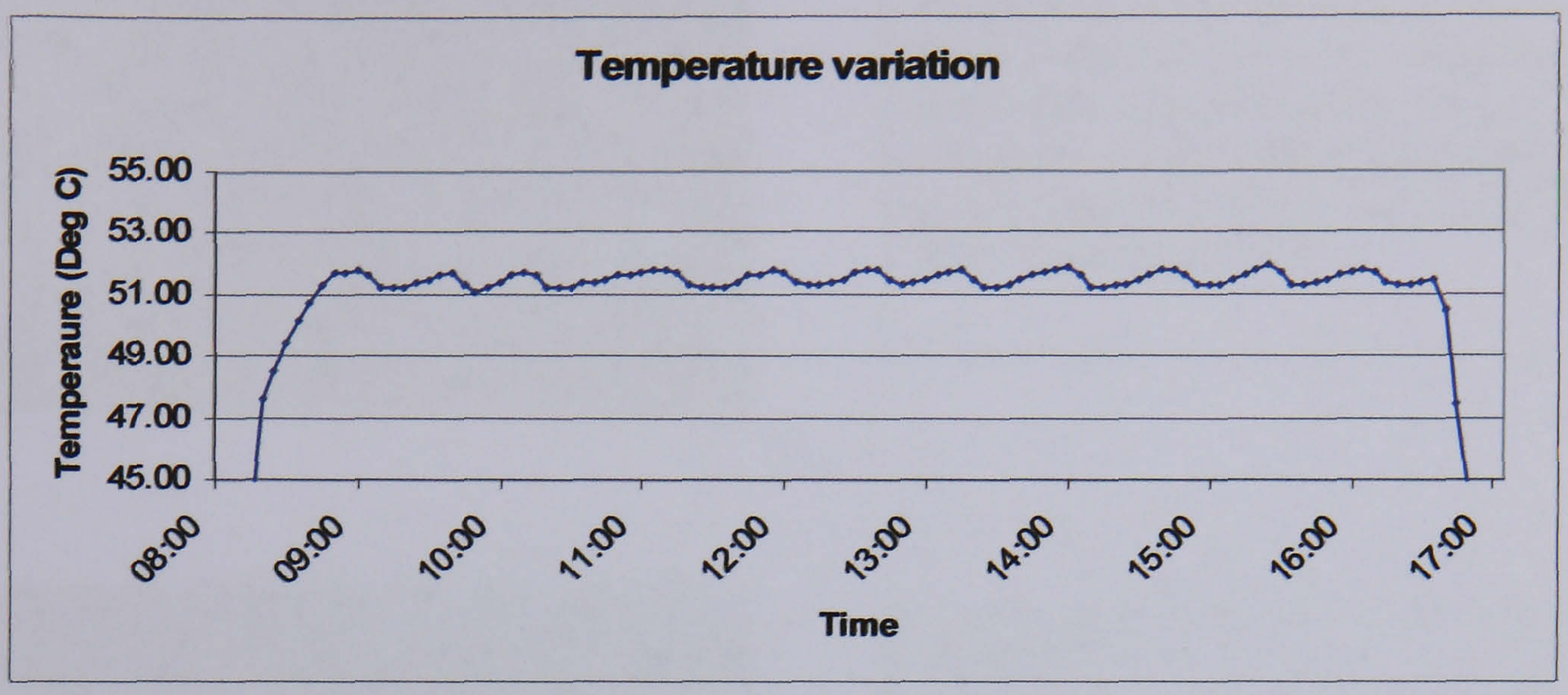


Figure 3.10 Temperature variations during normal machine operation, showing start and cool down effects and cyclic control during the day.

3.6 Surface Finish

The surface finish of a half-etched surface of a part is a very good indicator of the etching quality. In this study the average roughness (Ra) of sample panels was used as one indicator to determine the point at which the etchant had deteriorated to a state where it could no longer be used. A test panel was designed to confirm this at various stages of the research. This is described in Chapter 6. The surface roughness was measured with a Mitutoyo SP201P skid-less surface texture and measurement instrument, and is expressed in terms of micrometres (μm). The amount of free acid in the solution is thought to have a significant effect of the surface finish, but the relationship is complex and will depend also on the metal being etched [Allen, Hegart and Horne 1981]

For the tests conducted as part of this research, AISI 403S17 grade stainless steel was used and a good finish was determined as having a roughness of below 0.4 μm Ra. Any roughness above μm 1 Ra was considered as very poor, indicating that the etchant had reached the end of its useful life. Photographs of typical surfaces finish are shown in Figure 3.11 and 3.12.

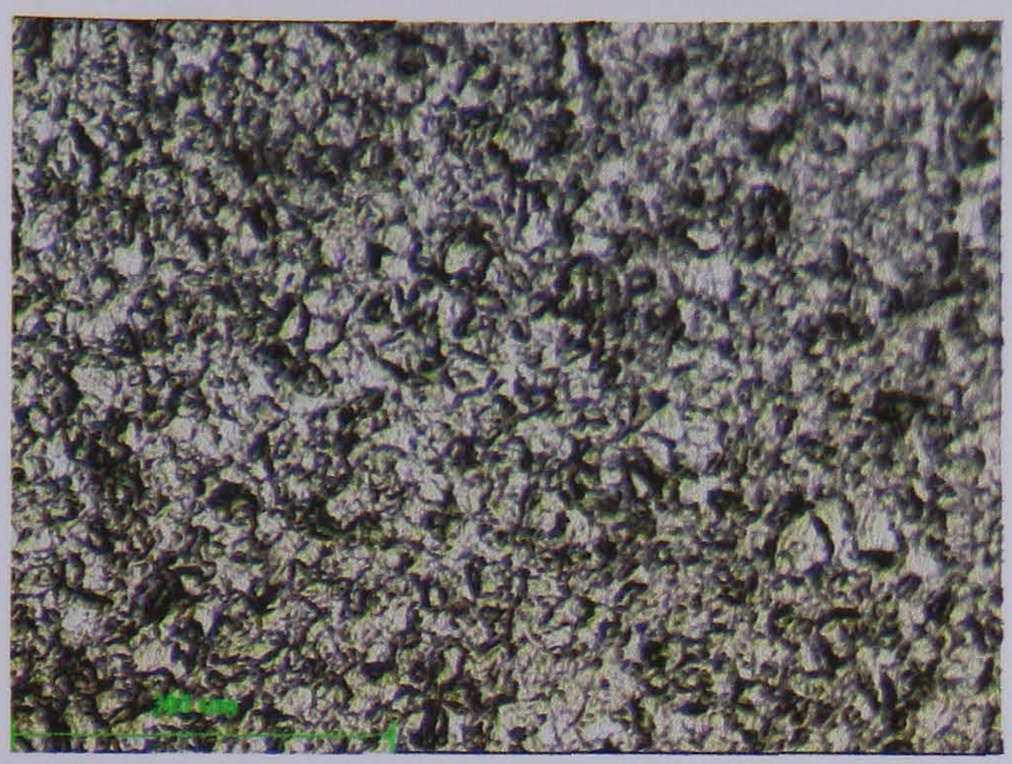


Figure 3.11

Photograph of part showing good surface finish – The surface is smooth and uniform and the Ra was measured as 0.4 µm. This is typical of a part etched with etchant in good condition typically with an ORP of 595mV and pH of -0.55.

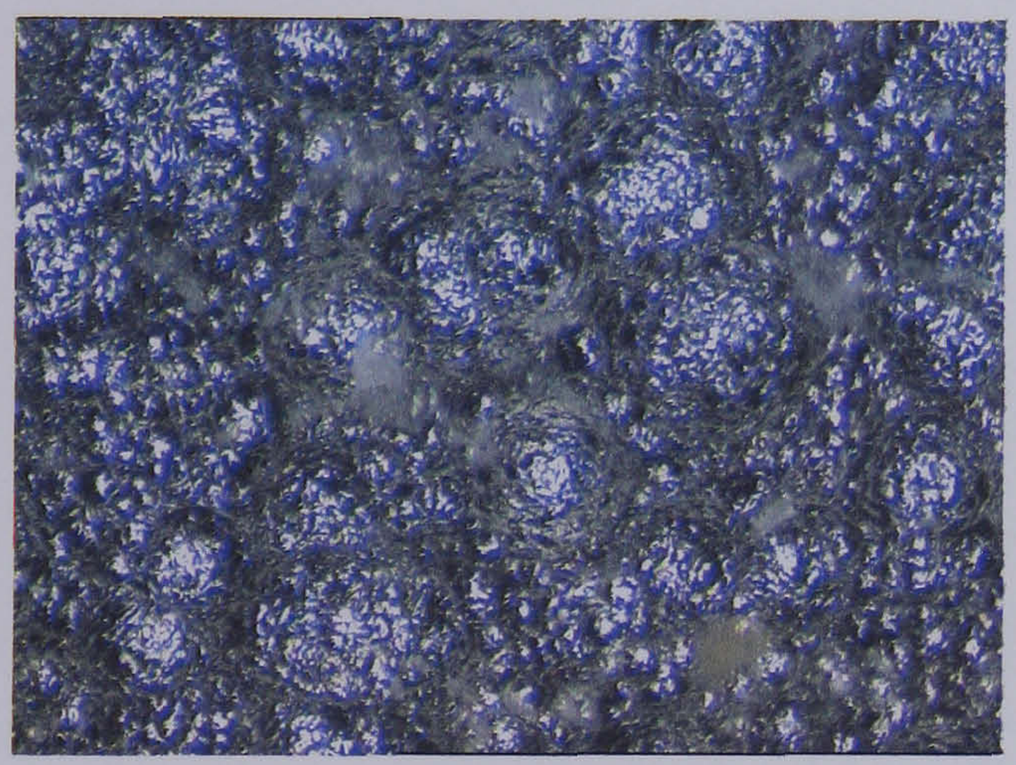


Figure 3.12

Photograph of part showing poor surface finish. The surface is very uneven and irregular and the Ra was measured as 1.9 µm This is typical of a part etched with etchant in a spent condition typically with an ORP of 550mV and pH of -0.1

3.7 Etch speed / Etch rate

The etch rate is defined as the rate at which the metal is removed. During use the activity of the acid will fall and hence the metal removal rate will reduce. The rate is normally expressed in micrometres per minute. At Tecan it is normally referred to as the speed setting of the machine to remove a standard depth of material. Conversions for the various methods used to express etch rate are given in Appendix 8. Therefore as the ferric chloride activity level falls the speed will reduce. The chart in Figure 3.13 shows the deterioration in etch speed as the ferric chloride ages in a machine with no regeneration. It is obviously desirable to keep the rate as constant as possible in order to maintain product size and productivity.

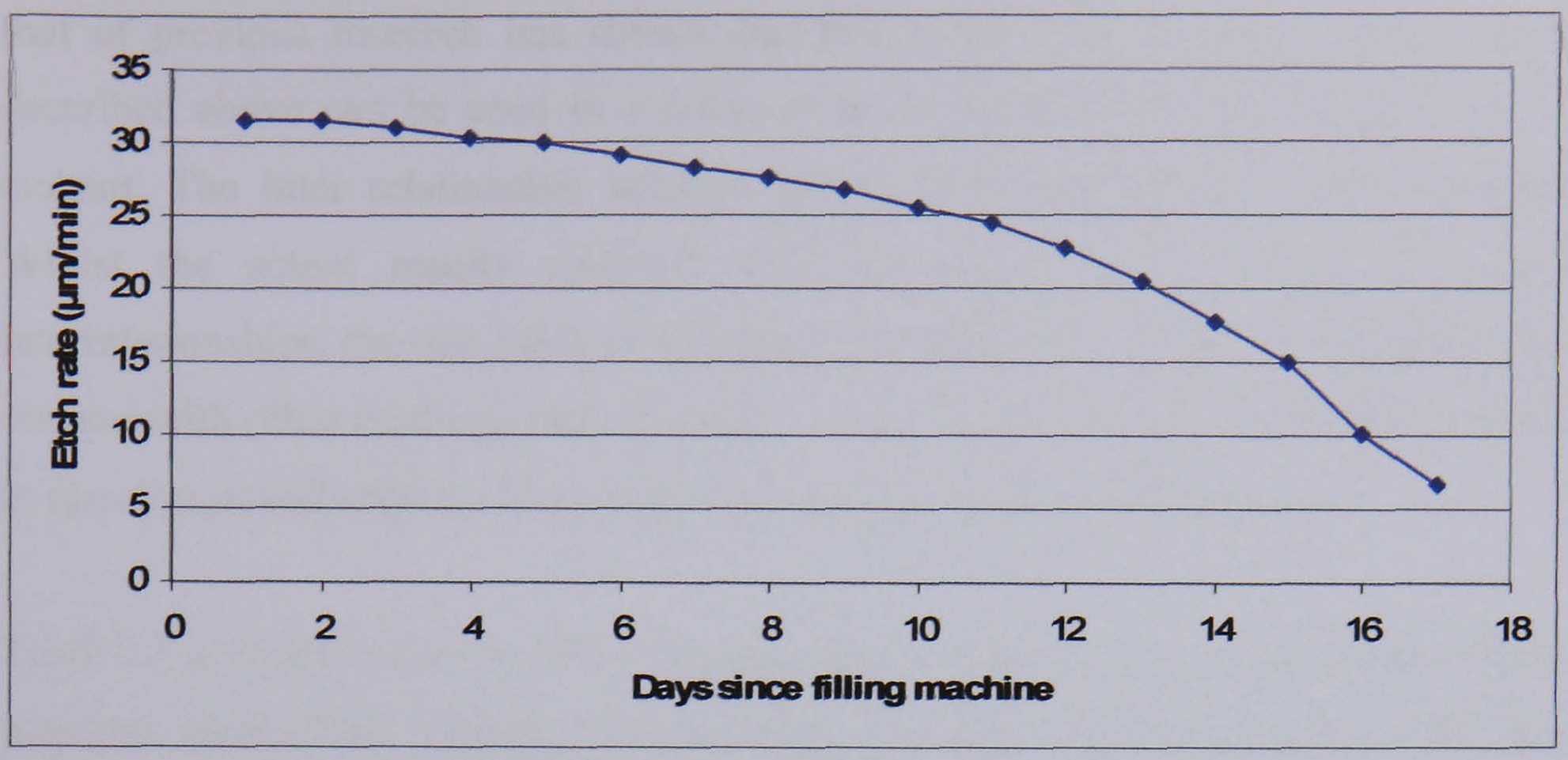


Figure 3.13 Typical reduction in etch rate as etchant ages

3.8 Effect of dissolved metal

As parts are produced, metal will be dissolved into the etching solution. This is certain to compromise the accuracy of any measurements made. A limited amount of research has been undertaken to determine the actual effect of these metals and possible monitoring methods for determining the metal loading using a microspectrometer. [Allen, Almond, and Maynard 2004]

In general, the conductivity of the solution will increase with metal loading, ORP will fall and, if no regeneration is undertaken, the free acid level will reduce. Similarly the °Bé of the solution can no longer be used as anexact measure of the concentration of the ferric chloride, since the reading will now be of the total metal loading of the solution from both ferric chloride and any etched metal byproducts.

3.9 Conclusion

In order to predict the etching characteristics of the ferric chloride etchant being used, it is essential that some form of scientific measurement is undertaken. For years the etching process has been considered as a 'black art' but the work undertaken during this study and

that of previous research has shown that this is far from the case. Basic techniques described above can be used in a commercial environment to indicate the state of the etchant. The inter relationship between many of the parameters must be considered. Whilst the actual results obtained may not always be 'accurate' due to these interrelationships, the true value of this type of monitoring comes from looking at them in context with other readings, thus forming a very useful 'snapshot' of what is happening to the etchant and what its likely behaviour will be when producing parts.

Table 3.1 gives an overview of the key parameters and indicates the interactions that exist between them. This clearly indicates that no single measurement can be used in determining the condition of the etchant. For example, when determining the ORP value of the solution the results obtained must be considered in conjunction with the free acid levels, increasing levels of which will suppress ORP. Similarly, if pH was used to determine the free acid levels, any changes in temperature must be taken into account. A number of key charts indicating these interrelationships are given in Appendix 9.

Parameter	Increasing free acid levels ▲	Increasing temperature (1) ▲	Increasing amounts of dissolved metals ▲	Increasing Baumé (1) ▲
Baumé	Falls ▼	Falls ▼	Increases ▲	-
ORP	Falls ▼	Increases ▲	Falls ▼	Increases ▲
pH	Falls ▼	Increases ▲	Increases ▲	-
Conductivity	Increases ▲	Increases ▲	Increases ▲	Falls ▼

(1) These parameters where kept constant during this research.

Table 3.1 Overview of the key parameters and the interactions between them

4. Equipment

4.1 Introduction

All of the tests carried out during this study were undertaken on an etching machine used in the daily production of parts in the sponsoring company. This was a Chemcut 547 double chamber etching machine with a sump capacity of 1000 litres as shown in Figure 4.1. In the machine work passes from left to right on a conveyor, a total of 224 spray jets are arranged evenly above and below the conveyor, the are fed with pressurised etchant. It is this spread and number of jets that allows work to be produced in a uniform way to tight tolerances. This machine was modified by the addition of two external pipe work circuits, one for solution sampling and one for chemical additions and mixing. Figure 4.2 gives a schematic overview of the complete installation. Complete details of the equipment used are given in Appendix 7 The previous study undertaken in 1999 by Peters used the same machine, but a number of problems and opportunities for improvement were identified both by Peters in his thesis and as a result of initial experimental work at the start of this study. These are dealt with in the following sections.

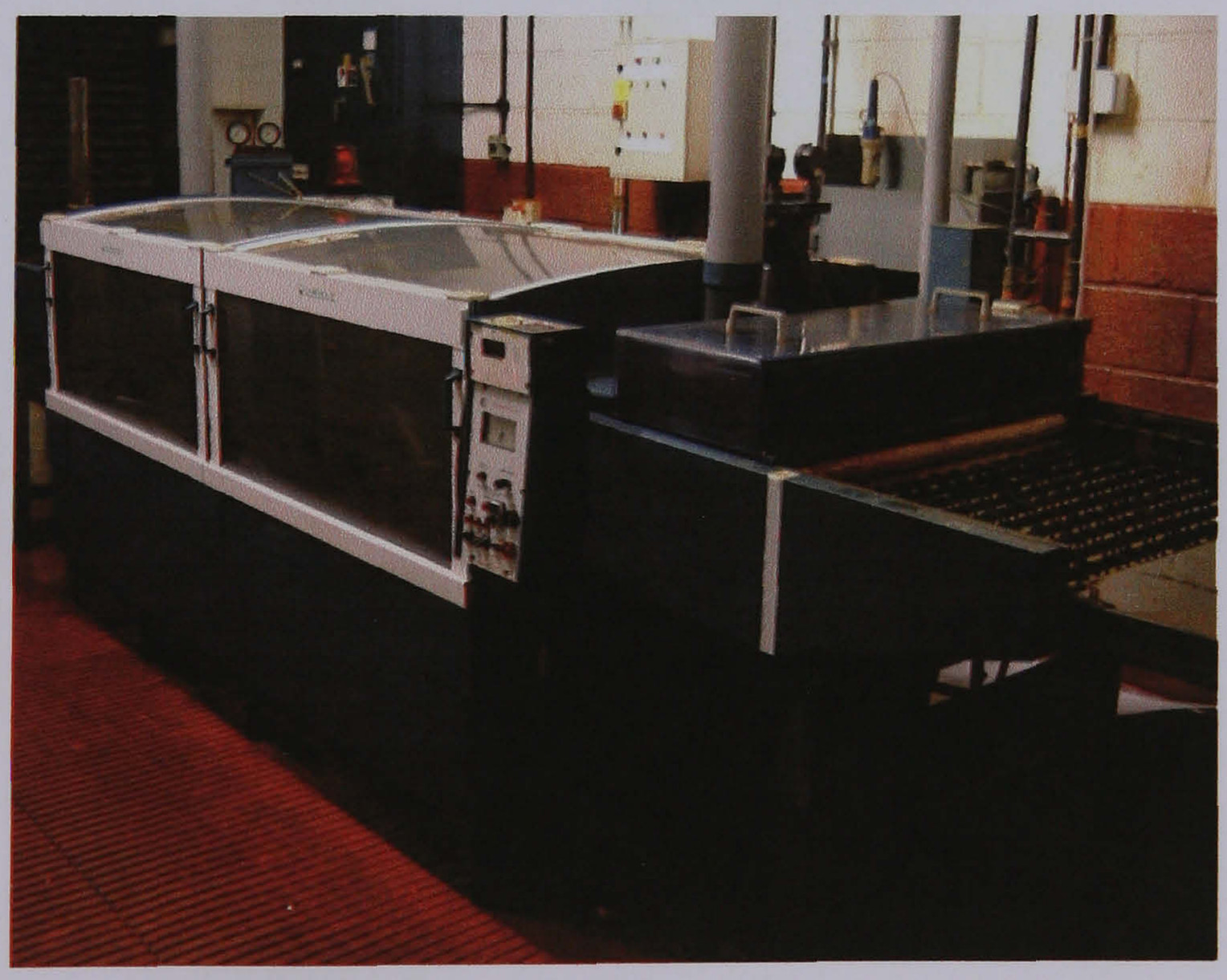


Figure 4.1 The Chemcut etching machine used for the experimental work.

The chemistry used in these tests was typical of that used in the etching process, i.e. a mixture of aqueous ferric chloride and hydrochloric acid. These were in daily use in the sponsoring company. Additions of oxygen were made as part of the regeneration tests. (Obtained from pressurised cylinders). Full details of the chemicals used are given in Appendix 10.

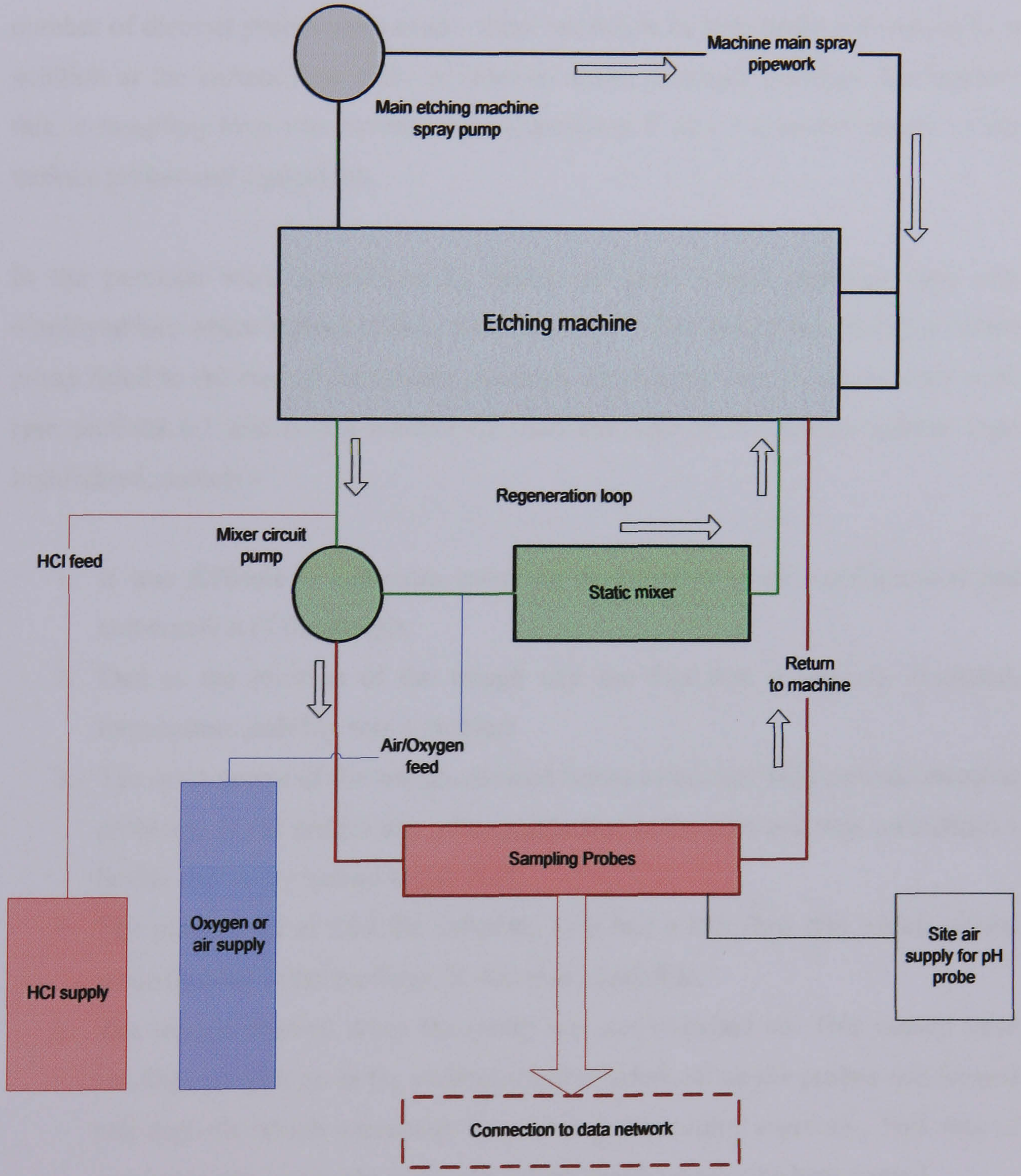


Figure 4.2

Schematic overview of equipment layout

4.2 Sampling loop

4.2.1 Problems with the previous design of sampling loop

In order to monitor ORP, pH and other parameters (see chapter 3) of the etchant a number of discreet probes were used – these needed to be constantly fed with etching solution at the correct flow rates in order to ensure accurate readings. To facilitate this, a sampling loop was constructed. Appendices 6 and 7 give the details of the various probes and equipment.

In the previous work undertaken by Peters, an open trough sampling loop was employed into which various probes were suspended. This trough was fed by a simple pump fitted to the rear of the etching machine. During the initial experimental work (see sections 6.1 and 6.2) a number of short comings of this simple system were highlighted, namely:-

1. It was difficult to add extra sampling devices due to the configuration and construction of the trough.
2. Due to the location of the trough and the fact that it was not insulated, temperature stability was a problem
3. The open nature of the trough allowed fumes to escape. This caused corrosion problems to the probes and other equipment in the area and was considered a health and safety hazard to the staff.
4. The pump used to feed the sampling loop had a low flow rate which caused some timelag in the readings. It was also unreliable.
5. The trough emptied when the pump was not switched on. This caused false readings on start up as the etching solution dried out on the probes and formed salt deposits which prevented the probes from reading correctly. This was of particular concern to the pH probe which should always be kept wetted.

The pH probe used is of a very specific design; this is necessary due to the very acidic nature of the etching solution. It is essential, as part of the design of the probe, that it

is operated under positive pressure. It was found that in practice it was difficult to maintain the pressure needed in the pH probe. Pressure is required to ensure that the etching solution did not leech back into the probe and destroy the electrodes.

4.2.2 Revised design as used in this study.

To overcome these problems a new sampling loop was designed. (Shown in Figure 4.3). This was constructed of PVC pipe and was fed from a bleed point in the main etching machine spray pump feed. The design of the loop was such that when the pump was not running; ferric solution remained in the pipe thus ensuring the probes were always wetted. This reduced the risk to them becoming coated with a passive layer when not in use. Into this pipe fittings were added to accommodate the various sensing devices. In use the sampling loop was insulated to improve its temperature stability (the photograph in Figure 4.3 shows the sampling loop with this insulation removed). To overcome the pressure loss problem with the pH probe a compressed air supply was fitted to it. This was fed via a pressure regulator from the company's site supply.

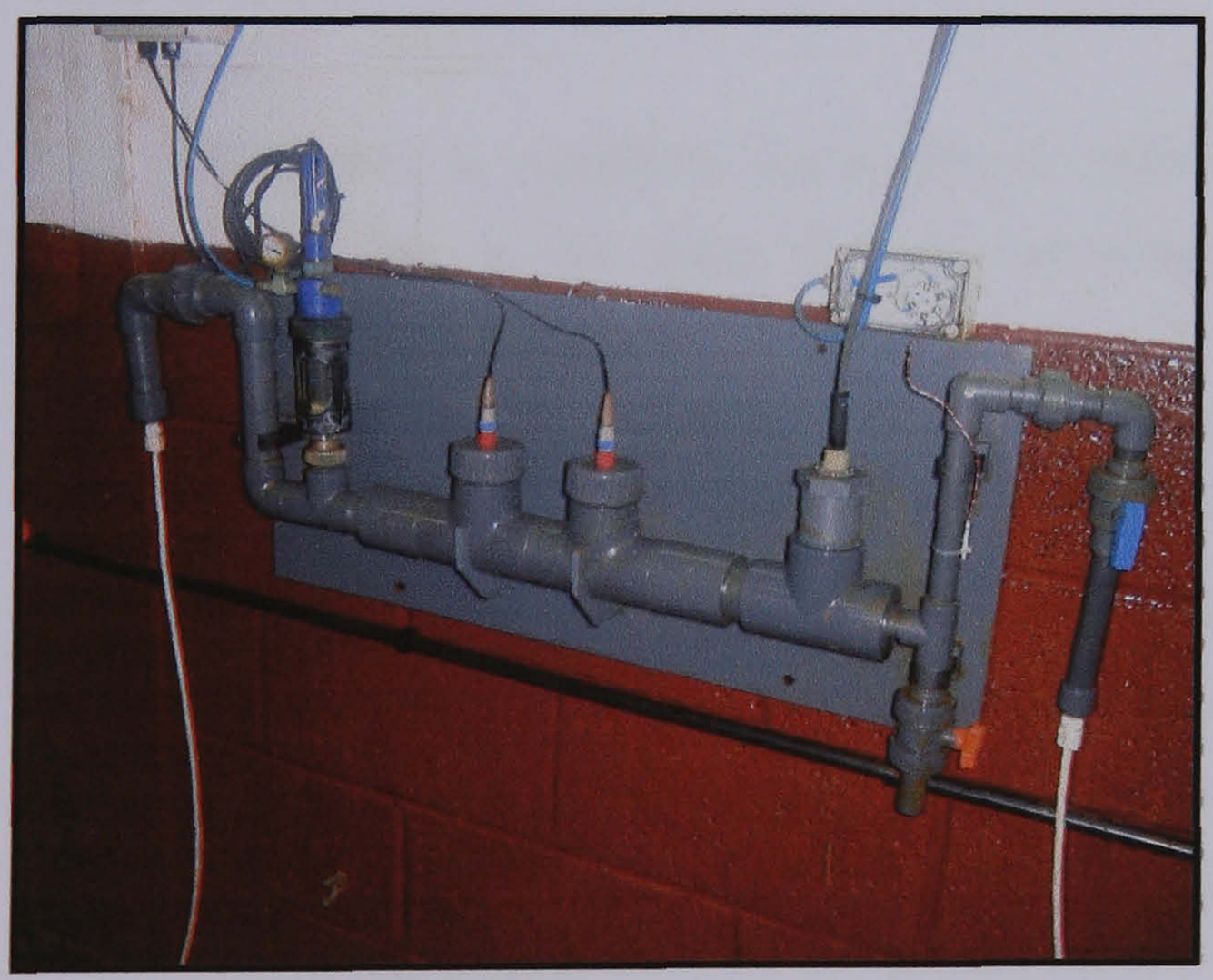


Figure 4.3

Modified sampling loop – showing (from left to right) probes for pH, ORP, temperature and conductivity. (Insulation removed)

In addition to those devices used in the previous work, an extra probe was added to monitor conductivity. The reasons for this are given in section 3.4.2.

During the experimental work undertaken in this study, further change was made to allow this sampling loop to be run from the mixer pump rather than the machine pumps which run the sprays in the machine. This improved the response time and stability of the system. This change also allowed monitoring to take place when the machine sprays were not running. This was particularly important as some tests were carried out overnight when normal production was not operating.

4.3 Computer system improvements

4.3.1 Review of previous system and the problems associated with its use.

The work undertaken by Peters used a PC based computer system to record the data collected from the various probes, carry out the analysis and control the operation of the oxygen and hydrochloric acid injection. Whilst this operated well during the initial experimental work a number of problems were encountered as the work progressed. These included:-

1. Difficulties in modifying the system to collect data from new monitoring probes, due in the main to issues of connectivity and the programme modifications required.
2. The PC proved unreliable in the environment of the etching machine. Corrosion of the computer was a major issue and all attempts to cost effectively solve this problem proved unsuccessful.
3. It was not possible to monitor the system remotely. This was considered as a significant problem since many of the tests would need to be made over extended periods and it would not have been practical to monitor the system without this ability.

4.3.2. System design and selection

Research was undertake to ascertain what other control systems existed. The criteria for selection was determined as a system which

1. Could survive in the harsh environment of an commercial etching shop,
2. Would allow data to be stored for extended periods of time in a way that would be simple to interrogate
3. Allowed remote monitoring, preferably over a conventional business data network. Tecan operated an Ethernet system running over structured cabling.
4. Could easily be developed and adapted as the research progressed.
5. Was cost effective – the system had to fit within the budget of the commercial enterprise. For this element of the project a budget of £3000 was agreed.
6. Offered long term reliability. It was known that the test program would last for some years and it was essential that data could be recorded and stored with minimal effort over this time.

Using the above factors as guidance, research was undertaken, using the internet and personal contacts to find the most cost-effective match of the available equipment and system requirement. One issue which had to be taken into account at this point was the sponsoring company's desire to have a system which could not only record data from this experimental system but also other equipment and processes around the factory. Whilst this factor was taken into account, it was not felt that this requirement compromised the final selection.

Rockwell Automation was identified as a major player in the field of data capture and process control. They have a world wide reputation for product quality and reliability and are used by many OEMs. They also offer, probably, the widest range of equipment available on the market today. These factors coupled with the level of technical support available from Tecan's in-house technicians as well as Rockwell's own engineer made them a natural choice for taking the project forward.

Of the many systems Rockwell offer one based on their DeviceNet[tm] architecture was considered the most suitable. DeviceNet[tm] is a low-end, open network that provides connections between low level devices, in this case pH and other meters, and high level devices such as PLCs and computers. The DeviceNet[tm] network uses a common industrial programming language, called CIP (common industrial protocol) to configure, control and collect date from the various devices. Details of the various DeviceNet[tm] items used are given in Appendix 7.

The system offered the following advantages

1. Low installation cost
2. Ease of connectivity allowing third party devices to be configured quickly
3. Reliability of networking system, hence reduced down time due to communication errors
4. The ability to monitor and control the system remotely
5. Flexibility of cabling and control systems

4.3.3 Data system layout

A schematic overview of the system is given in Figure 4.4. The system gathers data from a number of discrete devices. The devices were pH, ORP, 2 temperature sensors and a conductivity meter. Full details of the various devices are given in Appendix 7 Whilst it may have been possible to connect some of the probes themselves directly to the network it was felt desirable that the actual readings were available at the machine. Leaving the various meters in place gave the most cost effective solution to this and the fact that the operators could themselves observe the data improved their understanding and trust of the new methods being tested. The fact that the discrete displays remained also allowed data to be recorded manually if the network failed for any reason. This was, however, never the case. Outputs from the various devices were fed to input modules on the DeviceNet[tm] cabling. These modules convert the 4 to 20

mV outputs to digital data which is transmitted to the data logging and control computer located some 150m away. The data collection computer was connected to the DeviceNet[tm] via a scanner card and Ethernet controller. This computer had two functions, firstly to collect and store that data and secondly to monitor the data and signal when the regeneration system should be switched on. This process used the same DeviceNet[tm] cabling, with switching devices attached to control the pumps. To allow easy access to the data for monitoring and parameter setting, a simple human interface program was used to develop a single screen which allowed both functions to be undertaken. A screen shot of this is shown in Figure 4.5.

The data collection system was in turn connected to the factory's local area data network. This allowed remote monitoring of the machine to take place from any computer terminal within the factory and also facilitate remote monitoring across the internet if required.

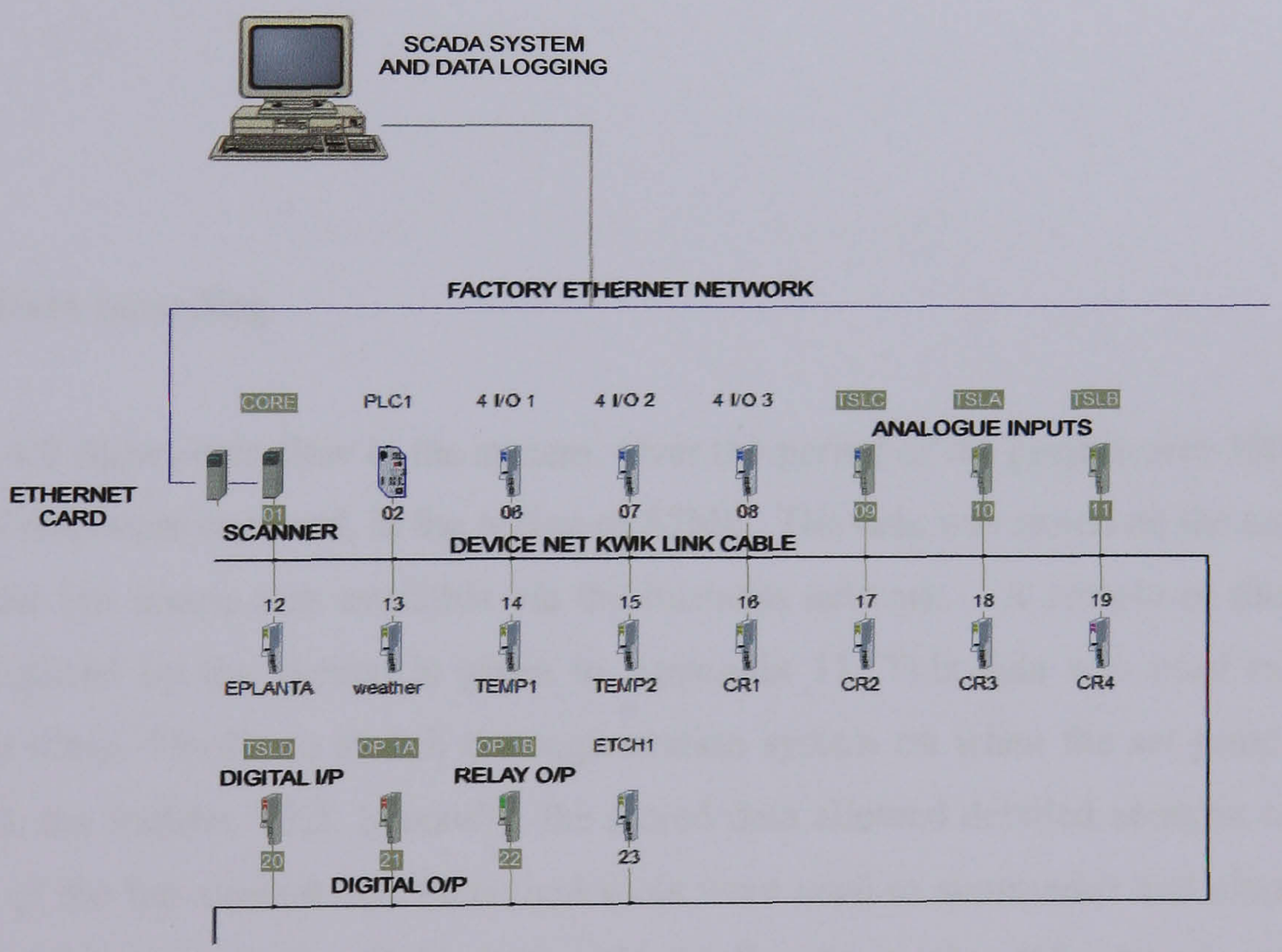


Figure 4.4 Schematic of date collection and control network

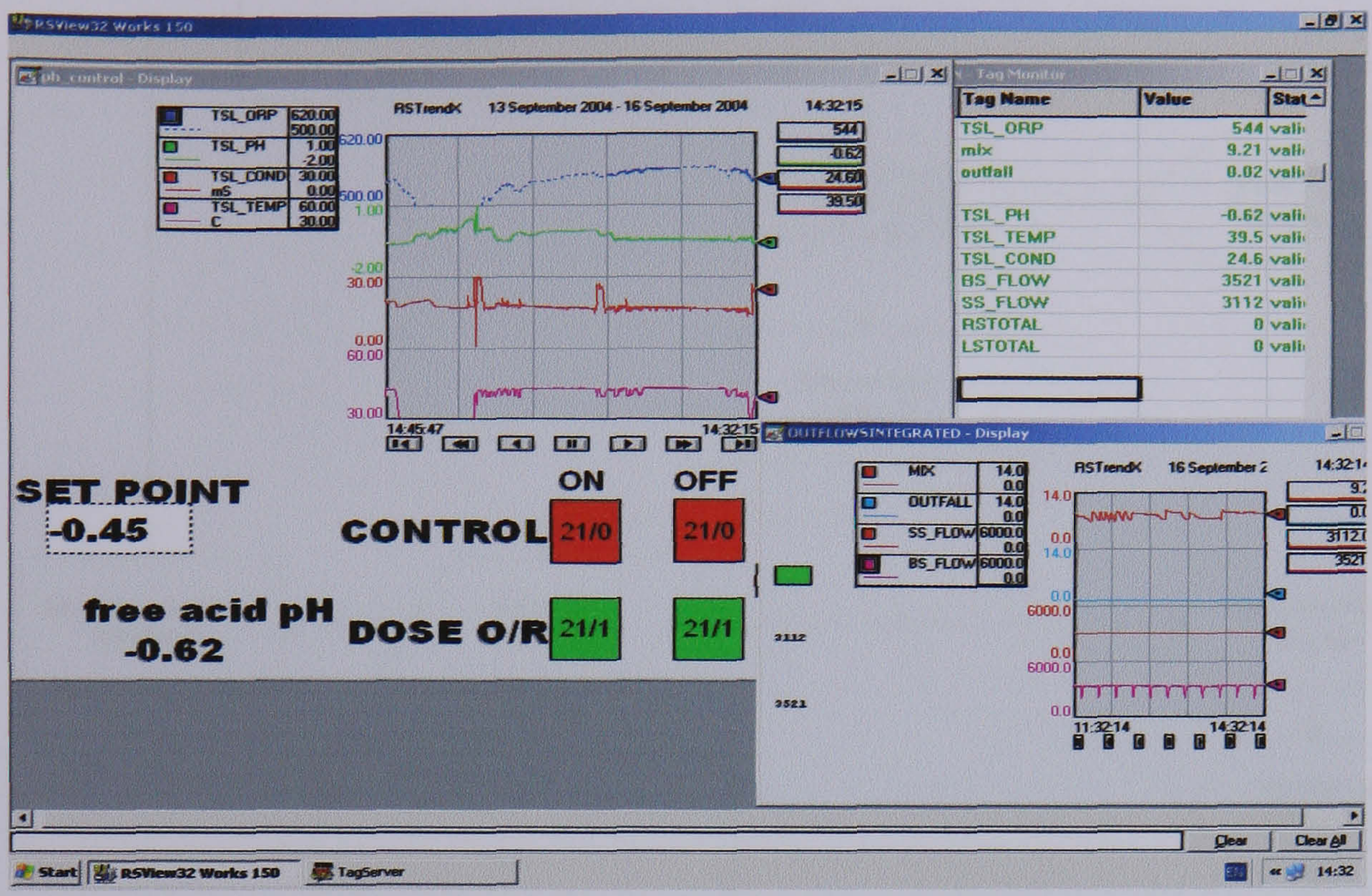


Figure 4.5 Screen shot of data monitoring and control system

4.3.4. Data recording

Figure 4.6 shows data flow in the system. Over the period of the project over 300,000 lines of data were captured, in the region of 85Mb. The data was stored on the control computer but access was available via the business network. A sample of the raw data captured by the system is given in Appendix 11. This data was used in two discrete ways. Firstly, to switch the regeneration system on when the set point was reached, see section 4.3.5. Secondly, the stored data allowed detailed analysis of the results of the test carried out. Statistical tools were used to summarise and chart the data; numerous examples of this appear in the Results section (Chapters 6 and 7). Overall, the methods employed to store and interrogate the data proved extremely satisfactory. Analysing data from experimental runs proved straight forward and it was easy to return to previously captured data in order to carry out further analysis as the research developed.

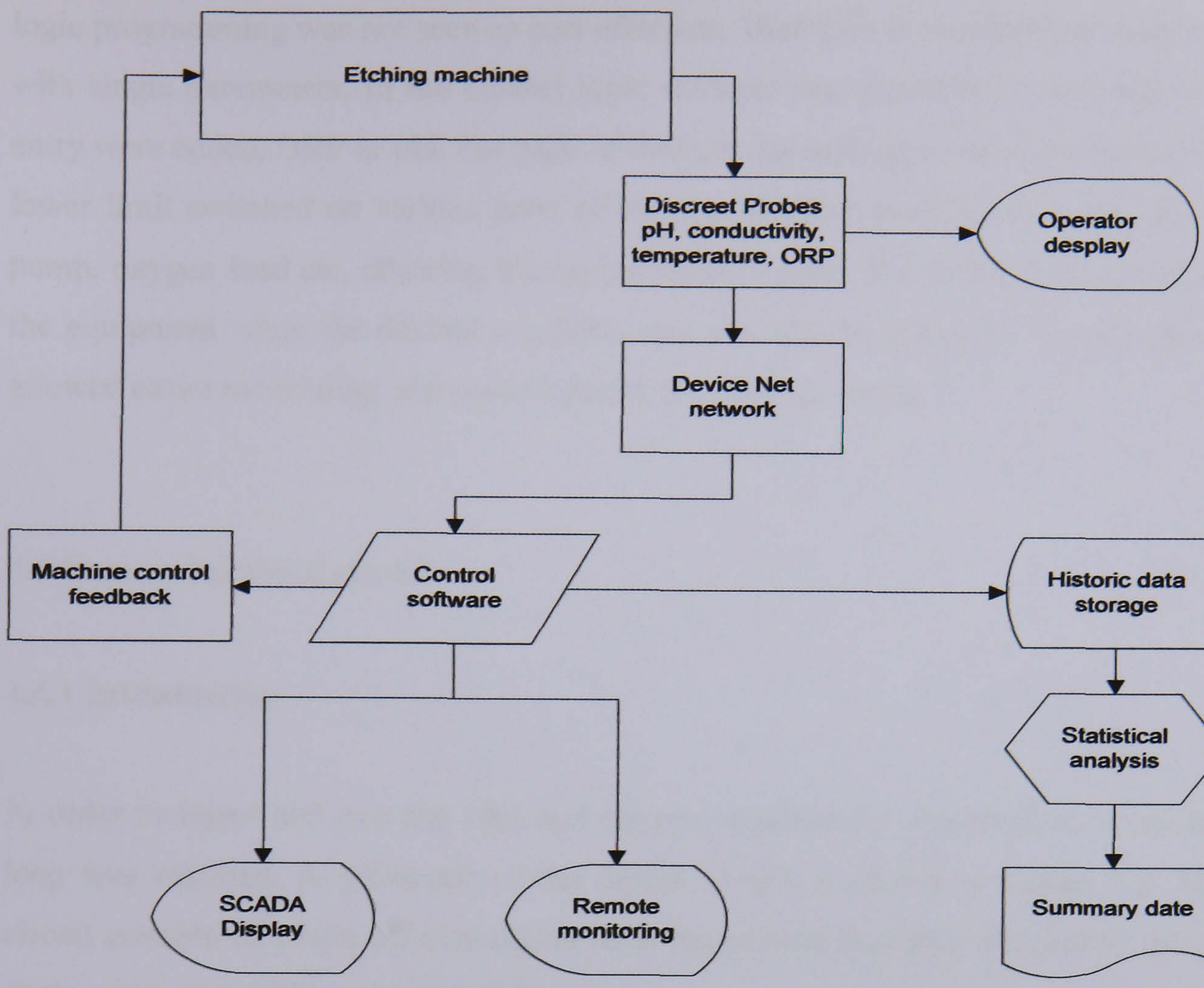


Figure 4.6 Schematic diagram of data flow

4.3.5 Control logic

The previous work by Peters had included a complex set of logic programs aimed at controlling both the ORP and pH within set limits. It was decided not to include this level of complexity in this study for two main reasons. Firstly the fact that, as shown in section 3, the ORP of the solution is affected by changes in pH which means that adjusting one parameter would cause the other to change irrespective of any actual changes in the solution. Therefore trying to keep both controlled within set limits would in practice prove very difficult, if not impossible, to achieve. Secondly none of the commercially available regeneration systems used complex control. Since the long term aim was to develop a system which could be sold commercially adding complex

logic programming was not seen as cost effective. Therefore it was decided to operate with single parameters. In the control logic software two possibilities for parameter entry were coded, ORP or pH. For each of these, lower and upper limits were set. The lower limit switched on various parts of the test injection loop, such as the mixing pump, oxygen feed etc, allowing the regeneration to start. The upper limit turned off the equipment when the desired condition was reached. Keeping the control simple allowed easier monitoring and control during the research work.

4.4 Oxygen Injection circuit

4.4.1 Introduction

In order to inject and mix the HCl and oxygen required for regeneration, a second loop was required. A schematic of the layout of this is shown in Figure 4.2. The circuit consists of a take off connection from the etching machine, circulation pump, static mixer and acid/oxygen injectors.

4.4.2 Static mixer.

This is a critical part of the regeneration system. Two separate mixing processes are taking place. There is a blending process of the two liquids, hydrochloric acid and ferric chloride, and a dispersion process of the ferric chloride and oxygen. The latter has a very high interfacial tension and in order to maximise the reaction, design and operation of the mixer is critical.

The mixer itself is a length of pipe into which an array of mixing elements has been inserted. Shear forces set up by the mixing element split the oxygen into fine bubbles. The aim should be to produce small and uniform bubbles and maintain these as long as possible to optimize the mass transfer process. The main advantage of this type of mixing is that there are no moving parts and it provides a very cost effective method

of mixing the ferric chloride etching solution with the oxygen and hydrochloric acid. A typical static mixer is shown in Figure 4.7. A cross section of the static mixer is shown in Figure 4.8 which clearly shows how the air (shown in red) is mixed into the solution as the solution travels form left to right through the pipe.

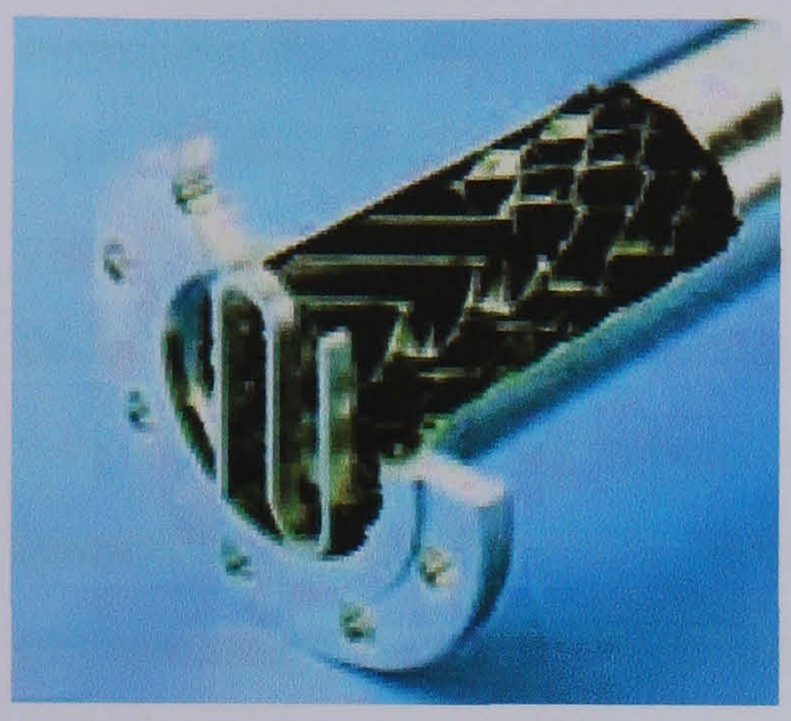


Figure 4.7

Cut-away section of static mixer showing mixing plates

(Photograph courtesy of Sulzer Chemtech)

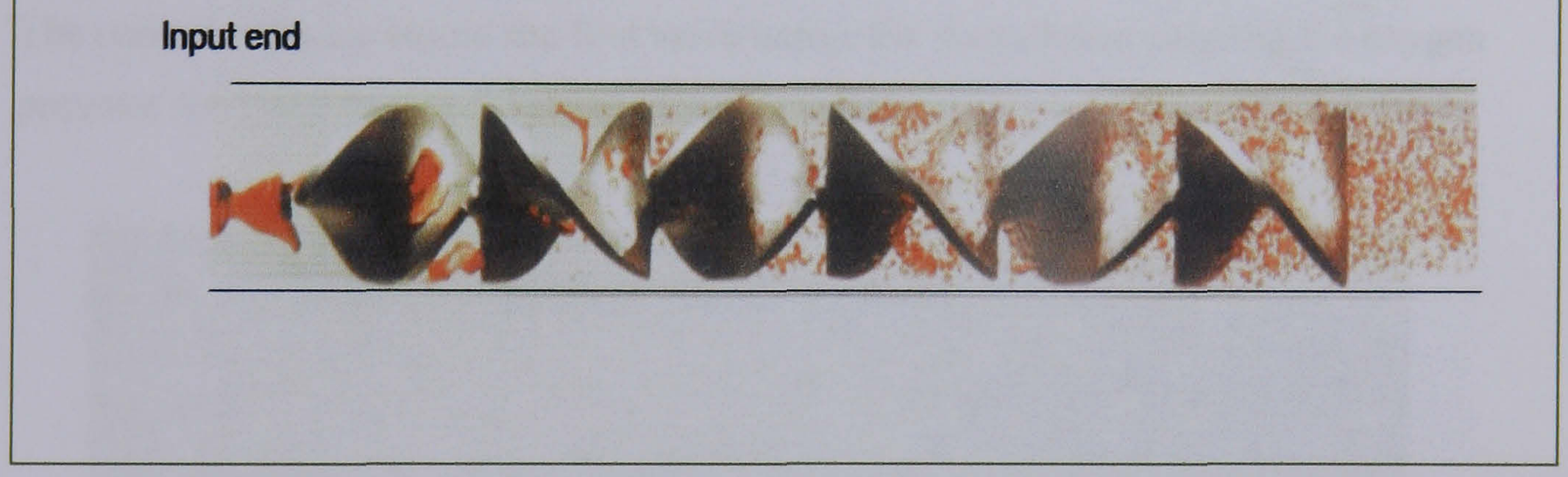


Figure 4.8 Cross section of static mixer (Photograph courtesy of Sulzer Chemtech)

4.4.3 Review of previous work and improvements made.

On reviewing the work carried out by A. Peters (1999) it was found that the position at which the hydrochloric acid was injected had not been optimised to allow good mixing. In Peters' work the HCl had been injected directly into the sump of the machine. There would have therefore been a considerable time lag until the free acid level had built up enough to allow regeneration to take place. In order to overcome this problem, changes were made to the injection circuit to allow HCl to be added immediately prior to the static mixer pump.

Problems had occurred during the previous study with ferric chloride solution leaking back into the oxygen feed pipe. It was found that the oxygen was being added immediately prior to the static mixer, on the pressure side of the pump. The non-return valve installed could not overcome the back pressure of the solution, which was in the region of 2 bar. This was deemed a serious safety hazard. In an effort to overcome this problem the oxygen was injected prior to the pump, on the low pressure side. Whilst this totally eliminated the problem of ferric chloride entering the feed pipe it caused problems with cavitations in the pump. During one test it completely destroyed the wet end of the mixing pump, the remains of which are shown in Figure 4.9. This problem was solved by moving the oxygen injection point to a position immediately after the pump. Whilst this was now on the high pressure side the issues of unwanted flows of ferric chloride back into the oxygen feed pipework were overcome by the addition of a second non return valve. One valve was located immediately prior to the injection point and one some 10m further down the pipe run. The control software closed the first valve before the second thus ensuring the oxygen pressure remained 'trapped' between the two valves.

Figure 4.9 Wet end of mixing pump – showing impeller 'welded' together due to cavitations

On review of the published data and during technical discussions with a number of equipment suppliers [Siddey 2004 and Sulzer 2004] it was felt that improvements could be made in the mixing process if an additional length of straight pipe was installed after the mixer prior to the return of the solution to the sump of the machine. This was achieved by re-configuring the mixing circuit. This review also noted that the static mixer had been used in a horizontal mode. In this mode it was felt likely that there would be an increased risk of phase separation after the mixing elements. This is clearly shown in Figure 4.10. As the flow changes from vertical to horizontal, bubbles can clearly be seen collecting on the top surface of the pipe. This phase separation will reduce the mixing efficiency considerably and slow the overall regeneration process. Tests were carried out with the mixer operating in both vertical and horizontal mode; the results of the various tests are given in Chapter 6.

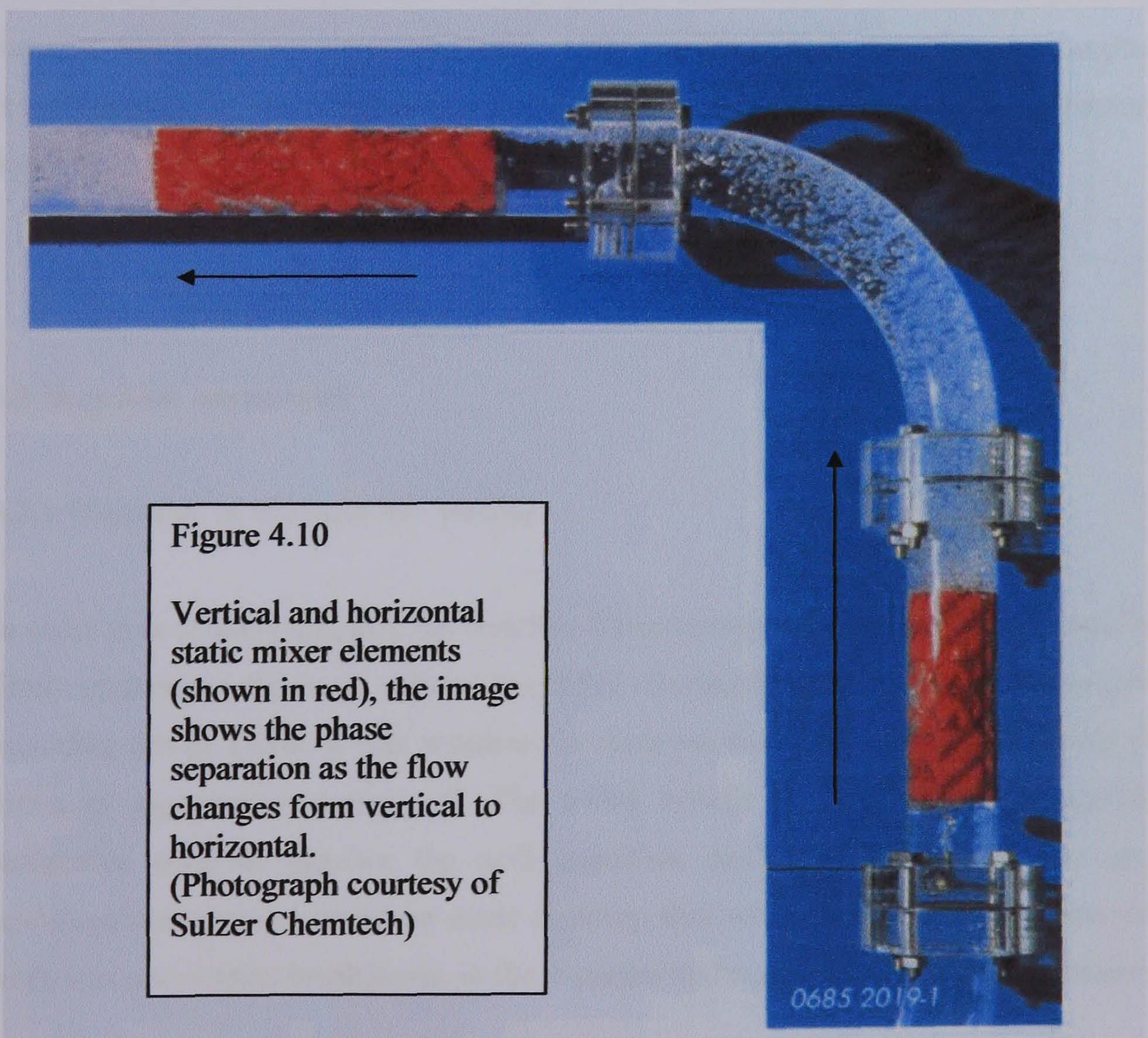


Figure 4.10

Vertical and horizontal static mixer elements (shown in red), the image shows the phase separation as the flow changes form vertical to horizontal. (Photograph courtesy of Sulzer Chemtech)

5 Experimental work

5.1 Introduction

The following sections detail the experimental research work undertaken as part of this study. All of the experimental work was undertaken in a production environment, using standard equipment which was being used to manufacture parts at Tecan. The work was centred on the etching process and used a Chemcut 547 double chamber etching machine, full details of which are given in section 4.1. The machine chosen for the study was one used to produce stainless steel surface mount printing stencils. This was selected as the work throughput was relatively uniform and the material being processed, mainly AISI 403 grade stainless steel was consistent. Details of this material are given in Appendix 12. It was felt that working with a fixed grade of material was important since this removed one variable out of what is a very complex set of parameters. The results and conclusions from this work are detailed in Chapters 6 and 7.

5.2 Base Line assessment

5.2.1 Objective of the base line testing

In order to accurately quantify the benefits of the regeneration process it is essential to firstly understand the costs without any form of regeneration. Since no data existed regarding this at Tecan, it was necessary to carry out a series of etching tests with all forms of regeneration turned off. The added benefit of these tests was that the equipment used to monitor the acid condition could be fully tested and any modifications required could be made ensuring that when the detailed experimental work was undertaken breakdowns in the experimental equipment could be minimised.

5.2.2 Base line test procedure

During these tests large sheets of stainless steel used in the production of surface mount component printing stencils (see Figure 5.1) were etched using Tecan's standard manufacturing procedures. Typically these are sheets 650mm by 610mm and on average 180 are processed per week.

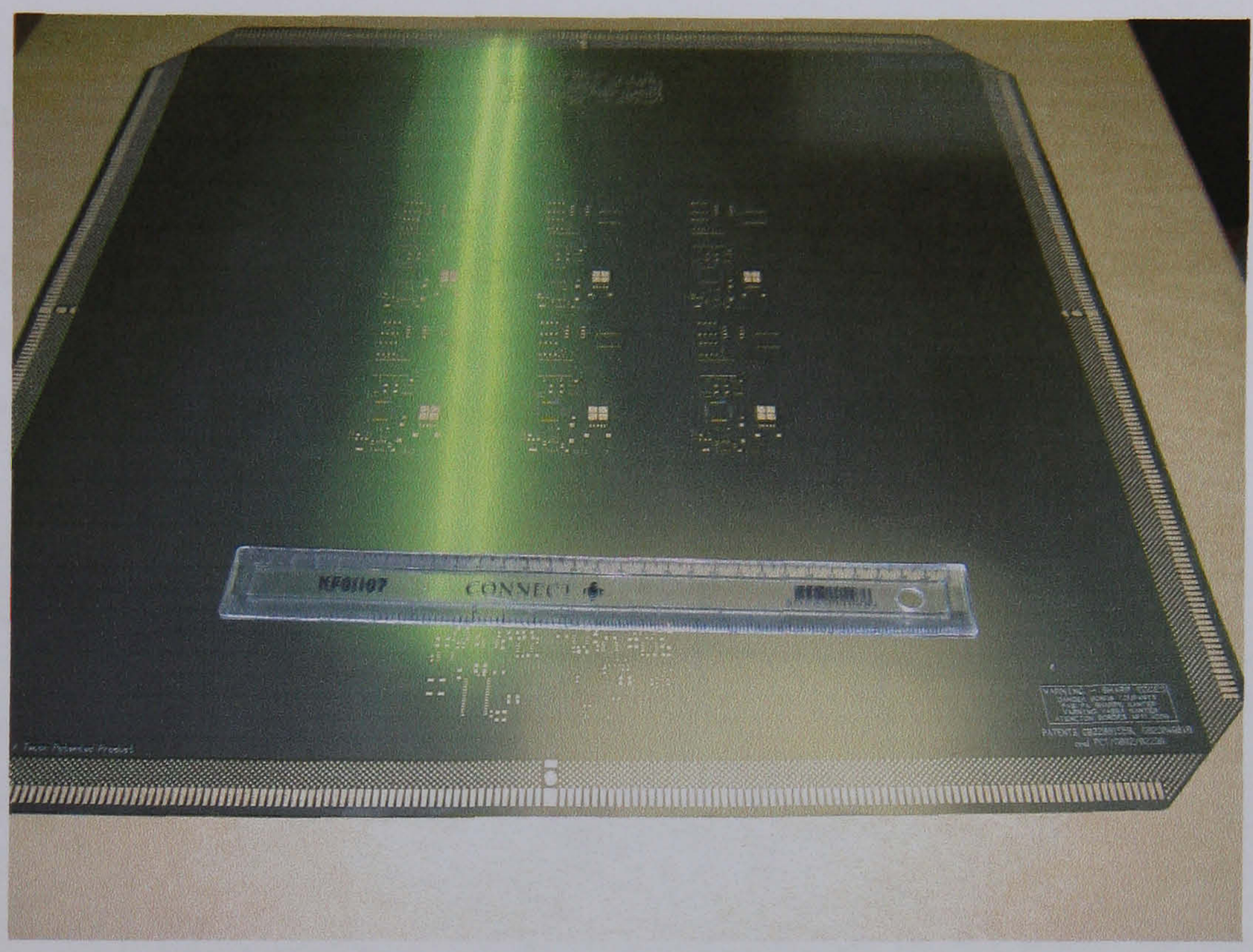


Figure 5.1 Typical Stencil component produced by Tecan

At the start of each test, the machine was filled with fresh ferric chloride. During this production the condition of the etching solution was constantly monitored and the readings for ORP, temperature and pH were recorded automatically using equipment developed during the previous research [Peters 1999]. It was obviously necessary to determine the amount of metal removed by the etching process. To do this, an average weight was calculated by weighing a number of sheets before and after etching. The quantity of sheets etched was recorded from which the weight of material removed could be calculated. The etch speed was also manually recorded by the operators.

Any additions made to the machine sump were also recorded. Typically these were additions of ferric chloride that were required to top up the sump of the machine. It was felt that the amount of top-up required was excessive and on investigation it was found that the anti-contamination rollers fitted at the end of the etch section were badly damaged. This allowed etchant to pass out of the etch chamber on the top surface of the etched blanks. The rollers were replaced but a small amount of acid was still seen on the surface of the sheets. After discussions with the machine supplier it was felt that this was inevitable, due to the nature of the product being produced. Figure 5.2 shows the blank and clearly indicates this problem in relation to the machine conveyor width.

The specific gravity of the solution was maintained as accurately as possible by manual additions of water; these additions were also recorded on the run sheet. An example of the manual recording sheet is given in Appendix 13.

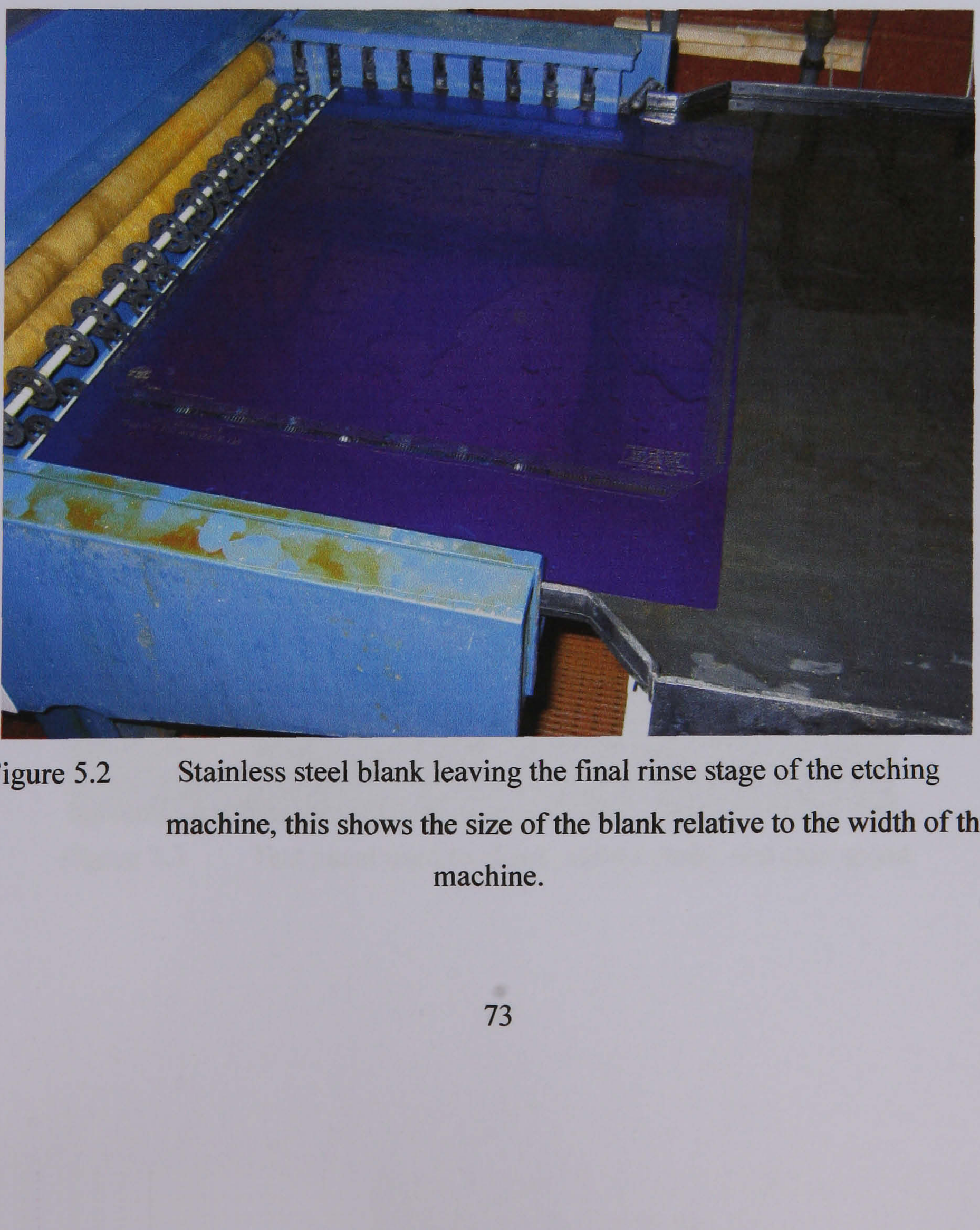


Figure 5.2 Stainless steel blank leaving the final rinse stage of the etching machine, this shows the size of the blank relative to the width of the machine.

The test run was continued until a point was reached at which the solution was deemed to be unusable for production. This was determined as the point at which the etch speed had significantly reduced and the profile around the etched features had deteriorated so far that the product produced would not be suitable for its intended use. The staff within the department made the initial assessment of this end point. However, to verify this and ensure repeatability a test panel was devised as shown in Figure 5.3. This panel allowed the etch speed, aperture appearance and size to be monitored and also facilitated measurement of surface roughness which was the primary physical parameter for determining when the acid had been exhausted. Panels were run at the start and end of every test and were kept as a permanent record of the quality of the finished product for reference and comparison during the study. In order to verify the result the experiment was repeated several times, each test taking around 4 weeks to complete. At the end of each test the acid was removed and disposed of. The machine was then cleaned and filled with fresh ferric chloride.

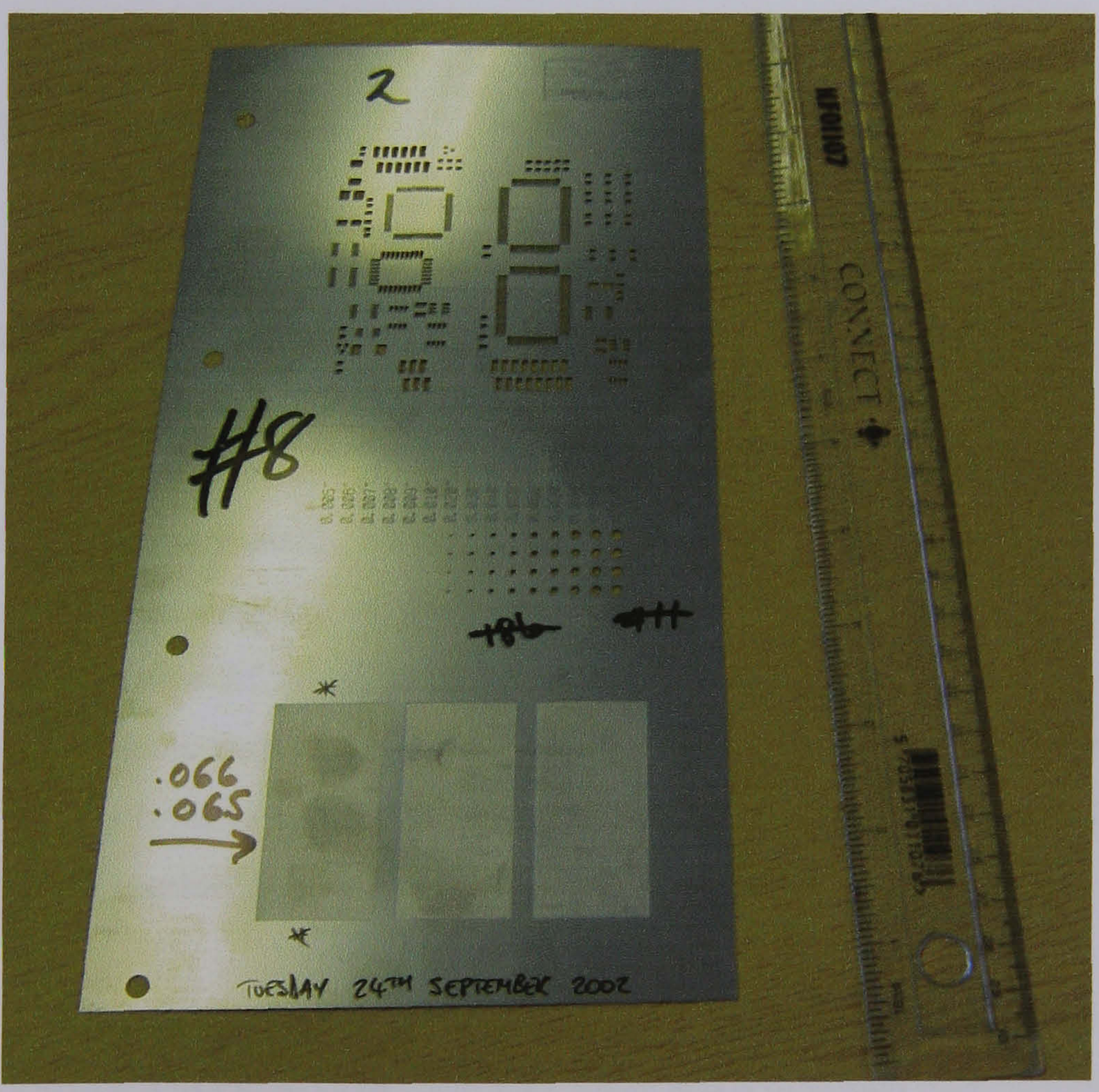


Figure 5.3 Test panel used to check surface finish and etch speed

5.3 Sodium chlorate and hydrochloric acid (BEAC) regeneration experiments.

5.3.1 Objective of the BEAC testing

In order to compare the oxygen regeneration results with the BEAC regeneration currently in use at Tecan it was necessary to accurately understand the actual costs of this form of regeneration in commercial use as compared with those which have been theoretically calculated, details of which are given in section 2.6. This part of the experimental work also allowed a review of the advantages and disadvantages of this regeneration method to be fully understood and documented.

As a result of the base line assessment experimental work a number of changes had also been made to the sampling system. Details of these changes are given in section 4.2. The BEAC series of tests also allowed these to be fully evaluated prior to the oxygen regeneration experiments.

5.3.2 BEAC Test procedure

Using the same standard etching machine and production environment used for the base line assessment experiments, tests were carried out over a nine week period. Initially the etching machine was filled with fresh ferric chloride; the BEAC was then set to control the OPR of the acid at a minimum of 580mv. During the test, production work was etched as normal. Some additional fresh ferric chloride was required to replace acid lost as drag out on the parts. Whilst this had been reduced, it was still present. The volume of metal removed and the quantities of chemicals used were recorded in the same way as that used for the baseline experiments. Test panels were run on a weekly basis to monitor the quality of the parts being produced and measure any changes in aperture appearance and surface finish of the parts.

The experiment was stopped after the nine week period. It was felt that sufficient data had been collected to allow analysis to take place and a thorough understanding of the operation of the equipment had by this time been gained.

5.4 Oxygen regeneration

5.4.1 Objectives of the oxygen regeneration experimental work.

It was intended that oxygen regeneration would form the major part of the experimental work undertaken during this study.

The objectives were split into 4 main areas

- To review the previous work [Peters 1999] and repeat the experiments carried out during that research, but over a prolonged period, the aim being to verify the results and determine what improvement could be made that would improve the overall efficiency of the system.

- To monitor the effect made by modifications to the control and mixing systems in line with the above, and to repeat the experiments such that the process could be optimised.

- Evaluate the use of air as a substitute to oxygen.

- To determine the operating 'window' for oxygen regeneration and production parameters.

- To develop a cost-effective monitoring system for ferric chloride etching equipment that could be used in a production environment.

5.4.2 Oxygen regeneration experimental work

An initial series of experiments was conducted over a one month period using the experimental equipment developed previously [Peters 1999]. These tests used oxygen and HCl flow rates used in Peter's research as well as those determined by the stoichiometric equations (details of which are given in Appendix 14). The test procedure was extensively the same as used in the baseline and BEAC tests. The machine was filled with fresh solution and ORP was used to initiate the regeneration

process. The machine was run for normal production, monitoring of the key parameters was undertaken and test panels produced for analysis. As with previous tests a manual log was kept of additions and weight of material removed.

Following this modifications to the injection system were made. These are described in section 4.4. The machine was then run, again with normal production. As the previous tests had revealed that not all of the oxygen being injected into the system was being used, variations in the flow rate of the oxygen and HCl were made to evaluate the impact this would have on the regeneration rate. Numerous tests were carried out at this point over a period lasting in excess of a year. Some of these were carried out overnight when the machine was not being used for production. The objective of this was to determine the reaction rate of the regeneration and identify any time delays which could occur between the additions of oxygen and HCl being made and regeneration taking place.

All of the modifications to the data recording system described in section 4.3 had by now been completed so it was possible to reliably record data continuously, day and night, and store it for analysis. Test panels were also produced to monitor the condition of the parts produced.

Following a detailed review of the configuration and use of the static mixer it was decided to modify the injection circuit further to allow it to operate in a vertical mode. On the conclusion of these modifications, additional test runs were conducted.

At this point, analysis of the results was pointing very strongly towards the importance of free acid level and was also indicating that the injection of oxygen was having little effect on the regeneration. It was therefore decided to run the machine with very tightly controlled pH and monitor the production and test blank output. This test continued for well over a year.

The results and analysis of this experimental research work are given in the following chapter.

6. Results of Experimental Work

6.1 Introduction

Following the experimental procedures described in the previous chapter the following observations and conclusions have been made. Due to the long term nature of this study and the monitoring systems used, it has been necessary to summarise many of the results. Therefore, the following discussion focuses mainly on general trends. During the course of the research some 85Mb of data were collected and analysed. This has been kept and will be available for future research.

6.2 Base-line assessment

6.2.1 Observations from base-line assessment

Using the monitoring and recording systems described in Chapter 4, data was captured for the critical parameters. From this data the following observations have been made.

Looking firstly at a typical single day's data, some initial instability of the pH and ORP readings was noted. This is shown in Figure 6.1. On investigation, temperature seemed to take some time to stabilise each day (as shown in Figure 6.2) and since temperature has a considerable influence on both ORP and pH, the majority of the instability could be explained by this. However, another factor which was thought to affect the initial readings was the coating which was seen to build up around the probes when not in use. This was 'washed' off after a short period allowing the probes to respond quicker to changes in the solution. These issues, coupled with the corrosion which was evident around the probe connections and the design of probe holder which allowed acid fumes to escape into the etch room, resulted in the redesign of the sampling loop described in section 4.2.3. For the base-line assessment work, the initial instability each day was excluded from the long term effects by eliminating this section of data each day.

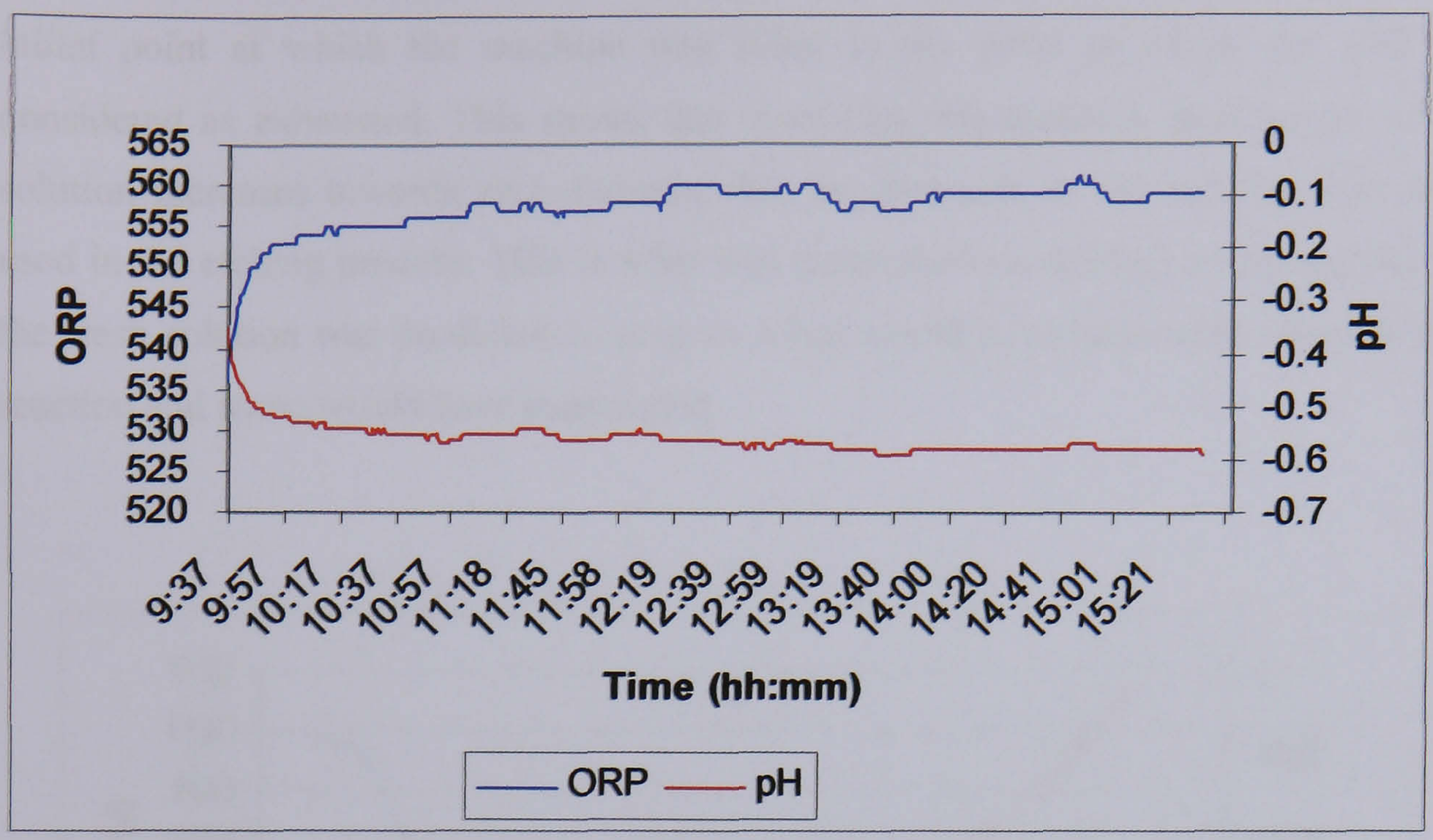


Figure 6.1 ORP and pH plots from a single day's data

(Results from test run on 11th Jan 2000)

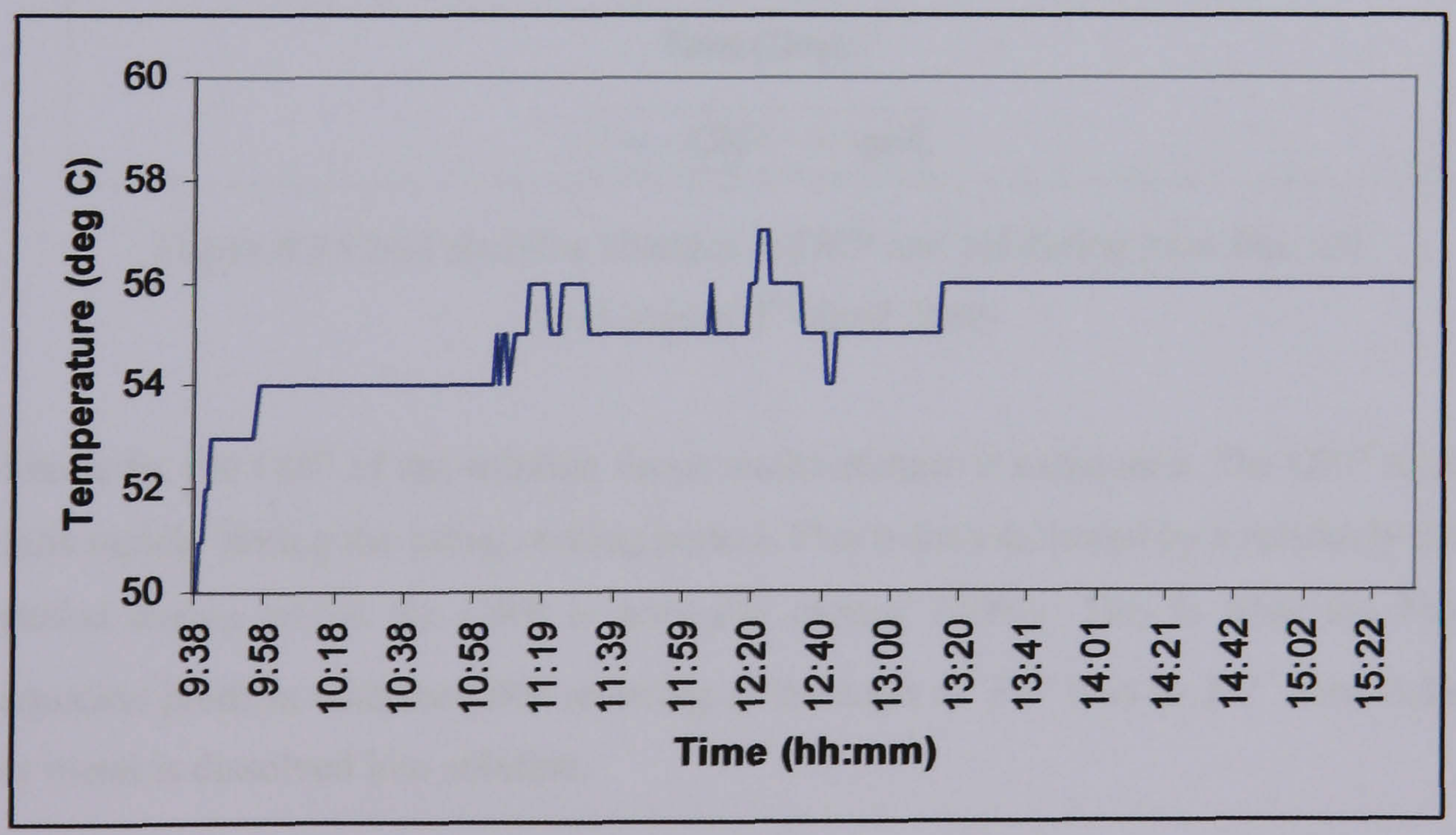


Figure 6.2 Temperature plot from a single day's data showing initial instability.

(Results from test run on 11th Jan 2000)

Figure 6.3 is a typical chart showing the movement in ORP and pH from the initial point at which the machine was filled to the point at which the acid was considered as exhausted. This shows that in etching the stainless steel the pH of the solution increases towards zero showing that the free acid in the solution was being used in the etching process. This is what was theoretically expected, as the free acid in the fresh solution was predicted to drop as some would have been used in the etching reaction and some would have evaporated.

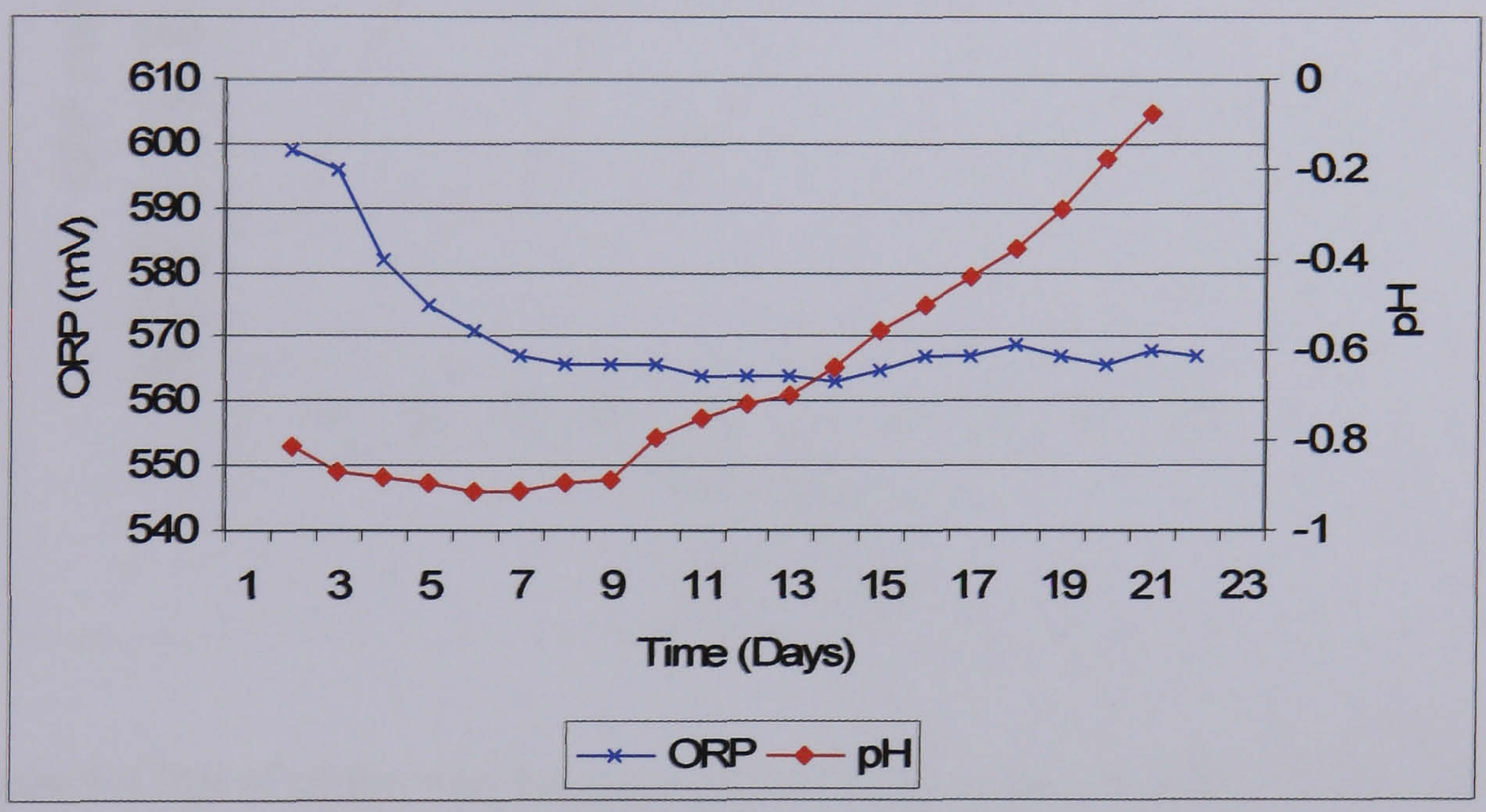


Figure 6.3 Chart showing changes in ORP and pH during base-line test

(Test started 3rd April 2000)

Similarly, the ORP of the solution drops as the etchant is exhausted. The ORP reading falls rapidly during the initial etching period. This is then followed by a relatively stable period during which the ORP is normally around 570mv. This is what the Nernst equation predicts with the ORP reducing as the ratio of Fe^{3+} ions to Fe^{2+} ions reduces as metal is dissolved into solution.

The results of the repeated tests are plotted in Figure 6.4. This shows that the ORP and pH follow largely the same pattern. However, the point at which the plot starts was very

different for the final two tests. This was believed to be due to variations in the concentration and make up of the fresh ferric chloride as it was received from the supplier. Despite this, the same trends were seen in these tests.

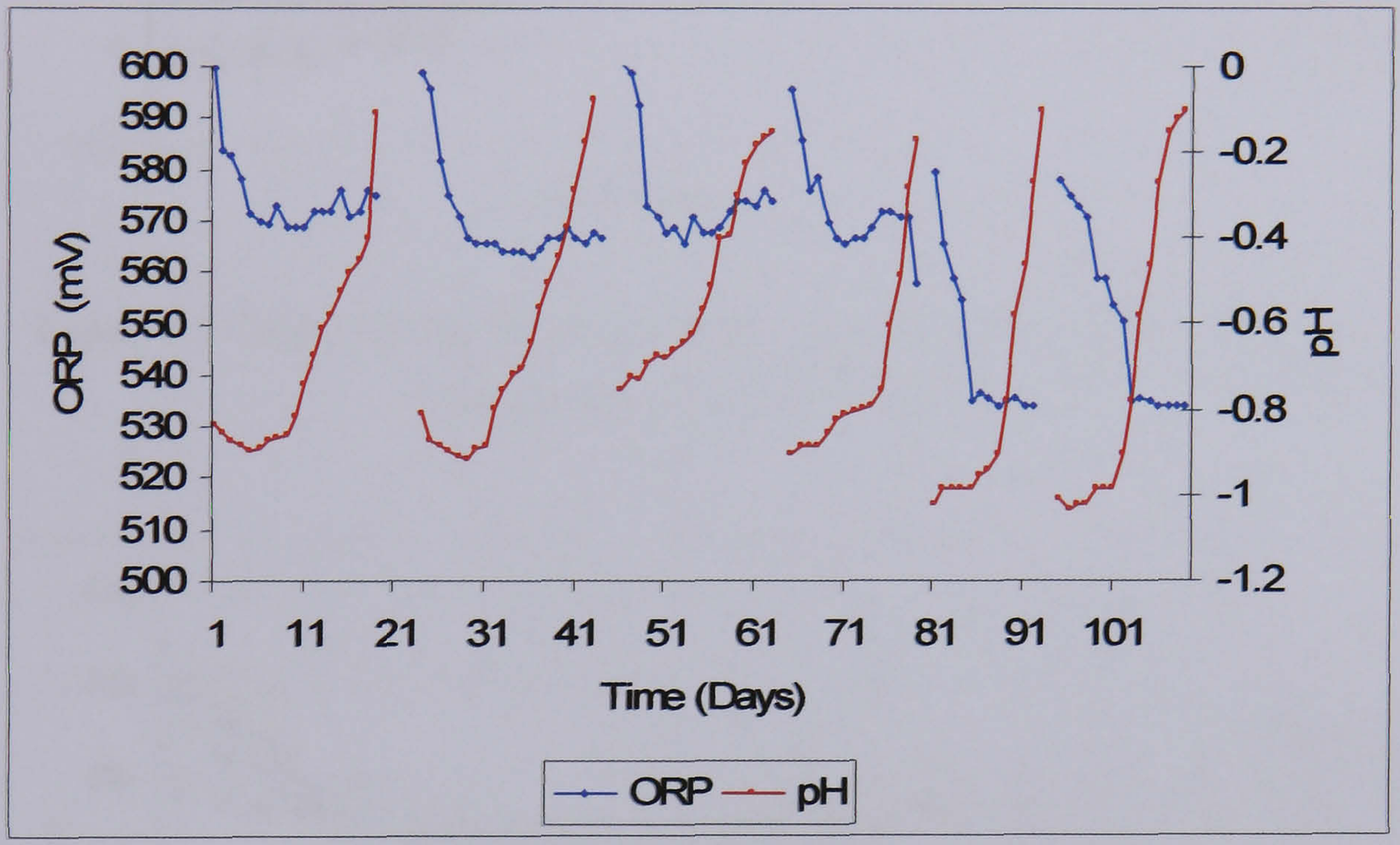


Figure 6.4 Plot of all the base line assessment tests showing the similarity in movement of ORP and pH *(testing started on 28th Feb 2000)*

By combining and averaging the results, general trends for ORP and pH of ferric chloride (which is not regenerated) can be deduced. These are shown in Figures 6.5 and 6.6.

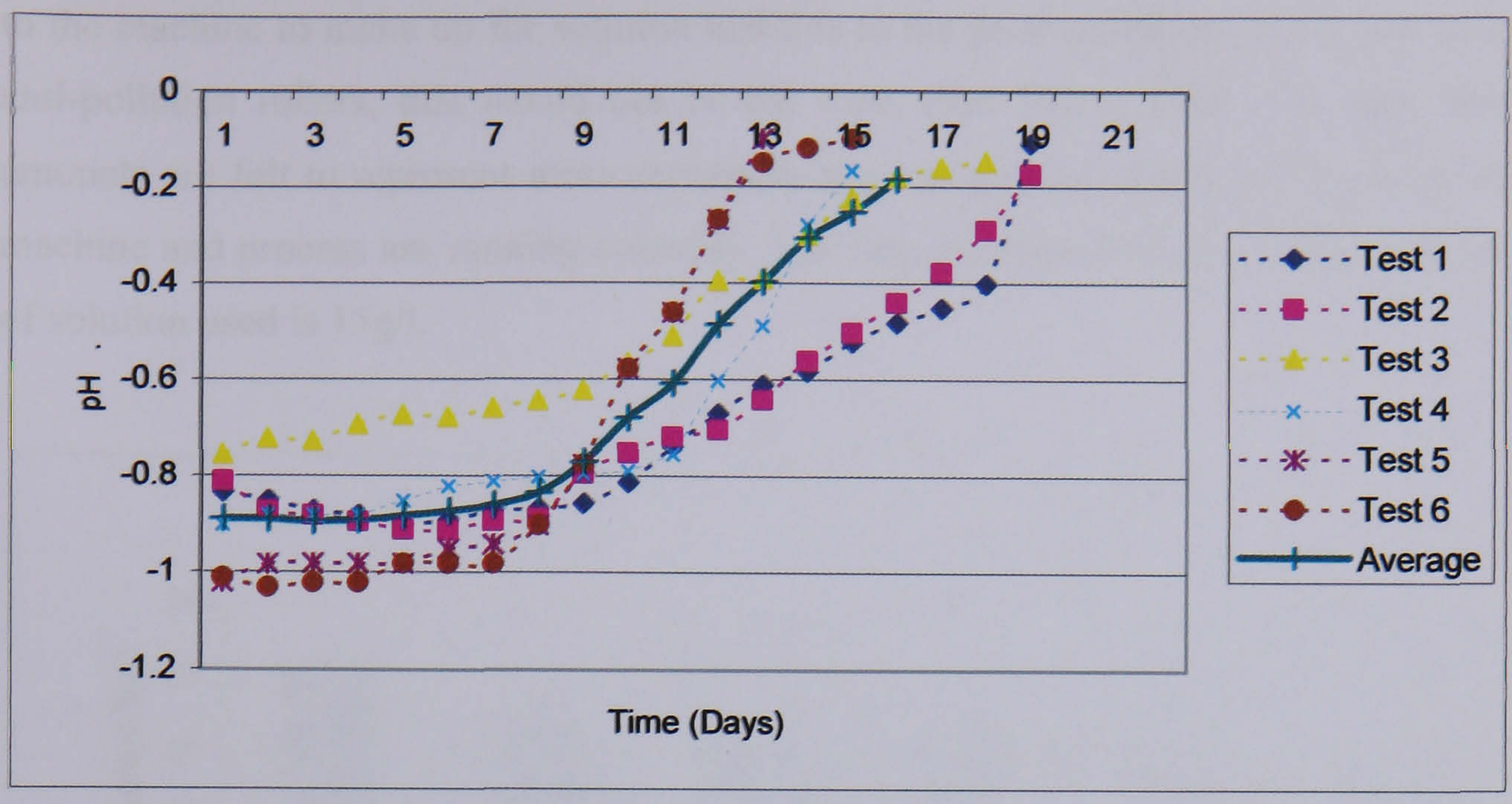


Figure 6.5 Chart showing the pH for each of the base-line test and average pH

(Testing started on 28th Feb 2000)

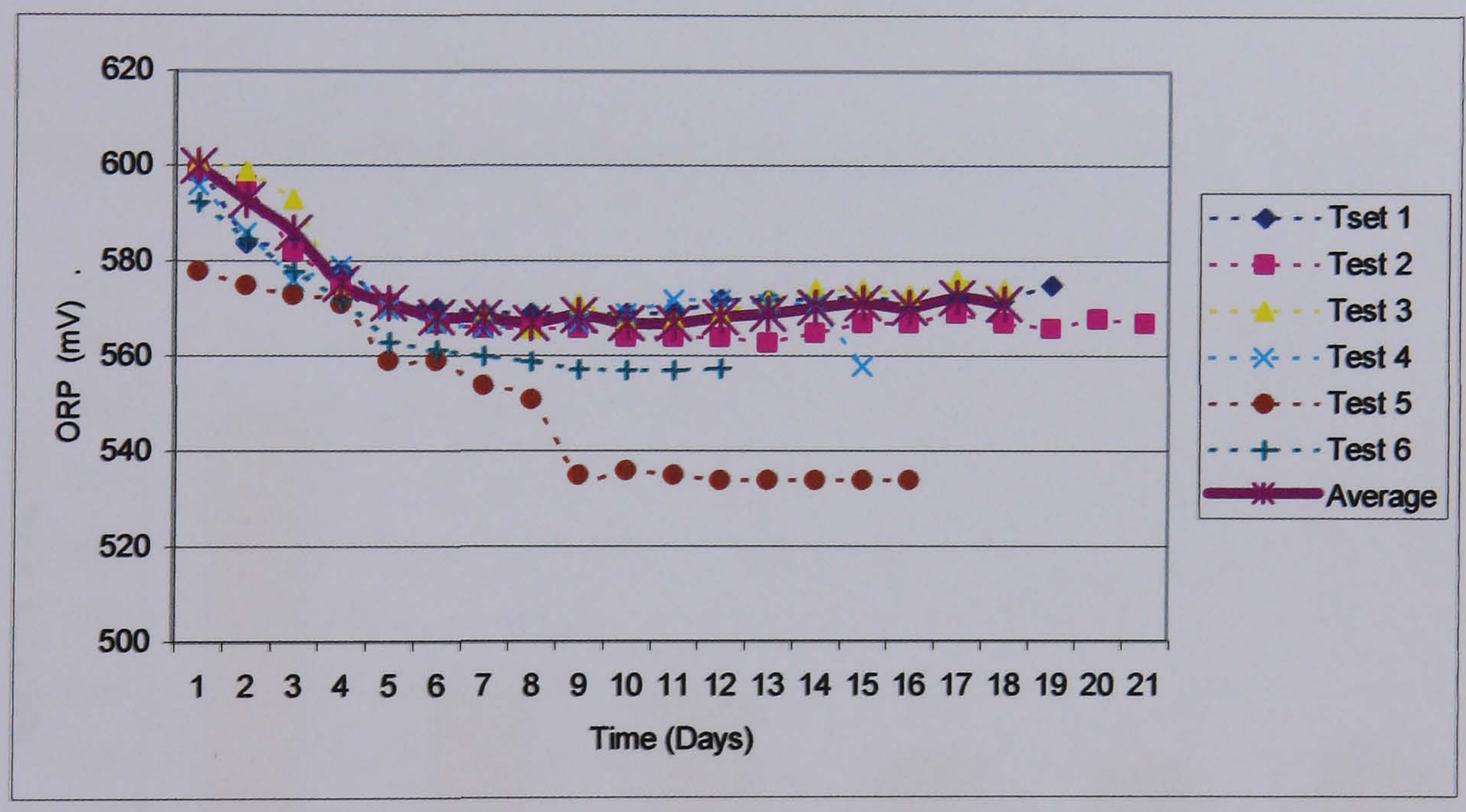


Figure 6.6 Chart showing the ORP for each of the base-line tests

(Testing started on 28th Feb 2000)

From the data recorded it was possible to calculate the weight of metal etched for each test run. This is shown in Figure 6.7 and indicates that the first tests had significantly more iron in solution when the acid was eventually believed to be exhausted. However, if these loadings are compared with the amount of additional fresh ferric chloride added

to the machine to make up for solution lost due to the poor condition of the machine's anti-pollution rollers, this would not be the case. (See Figure 6.8) The final three amounts are felt to represent more accurately the true picture of the loading when the machine and process are running correctly. The best estimate of metal loading per litre of solution used is 15g/l.

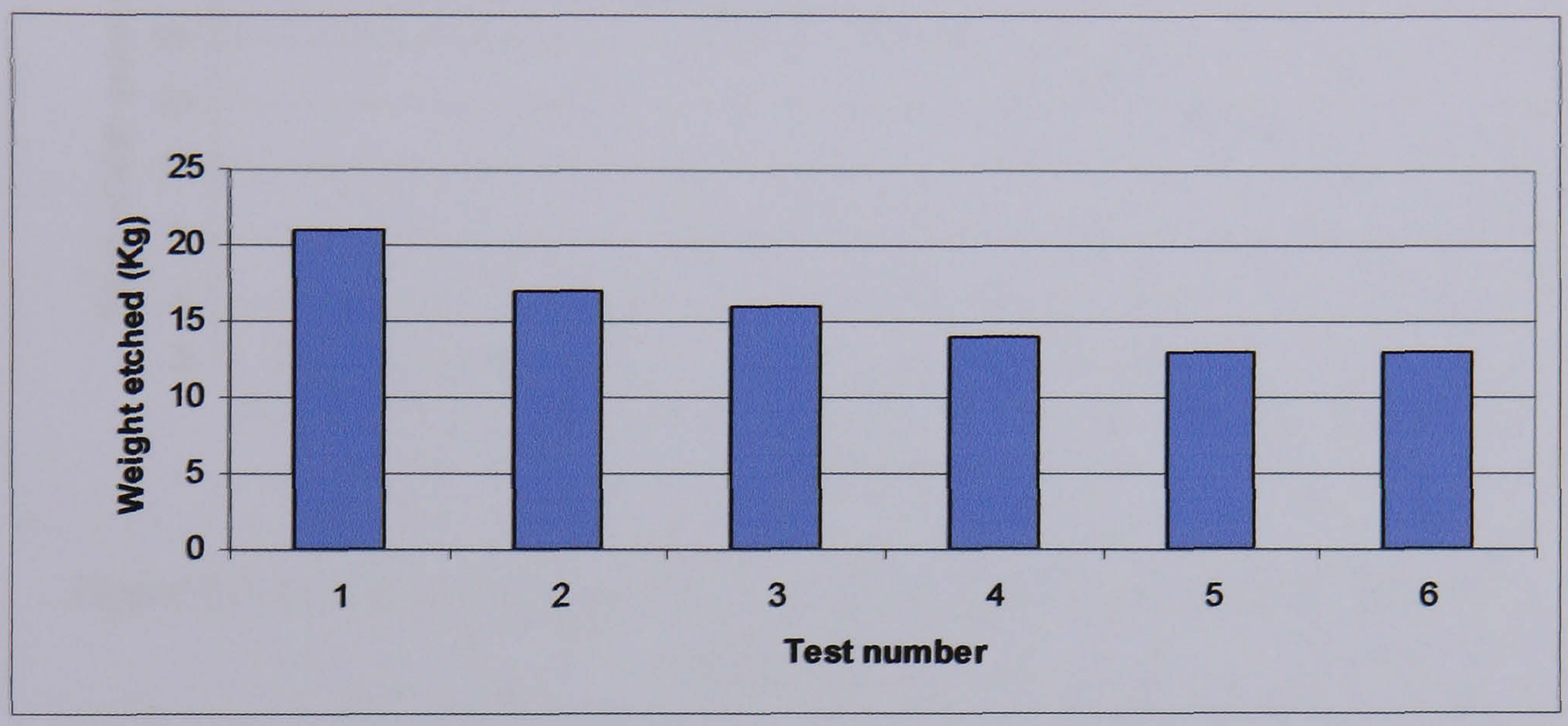


Figure 6.7 Total metal loading for each test run *(Testing started on 28th Feb 2000)*

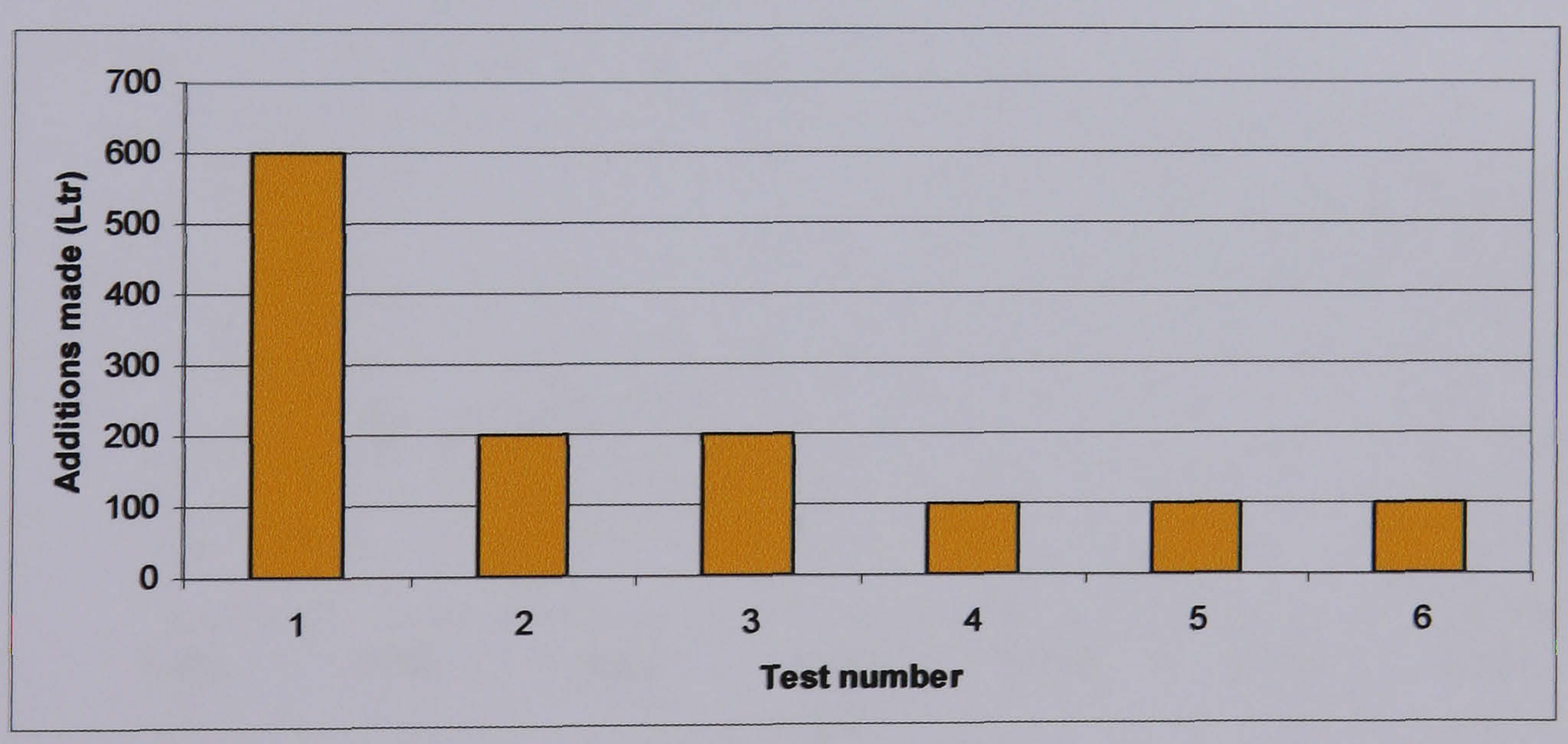


Figure 6.8 Amount of additional ferric chloride added for each test run *(Testing started on 28th Feb 2000)*

With regard to product quality and operation of the machine from a production view point, typical surface finish and etch speed charts are given in Figures 6.9 and 6.10. This again supports the previous research and literature.

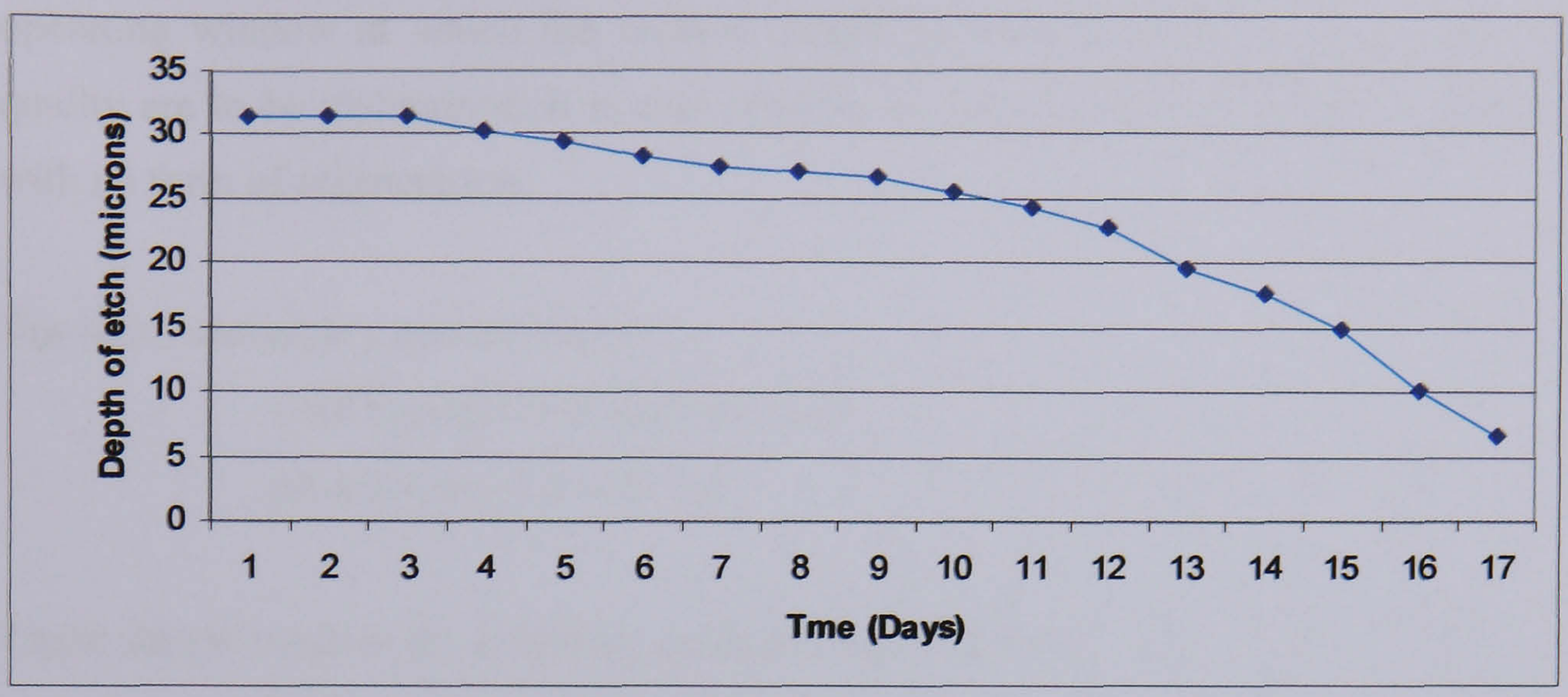


Figure 6.9 Typical etch speed chart showing reduction in etch depth as etchant is exhausted.

(Depth of etch refers to the amount of metal removed in a single pass through the machine with the conveyor fixed at a set speed of 2.25 m/min)

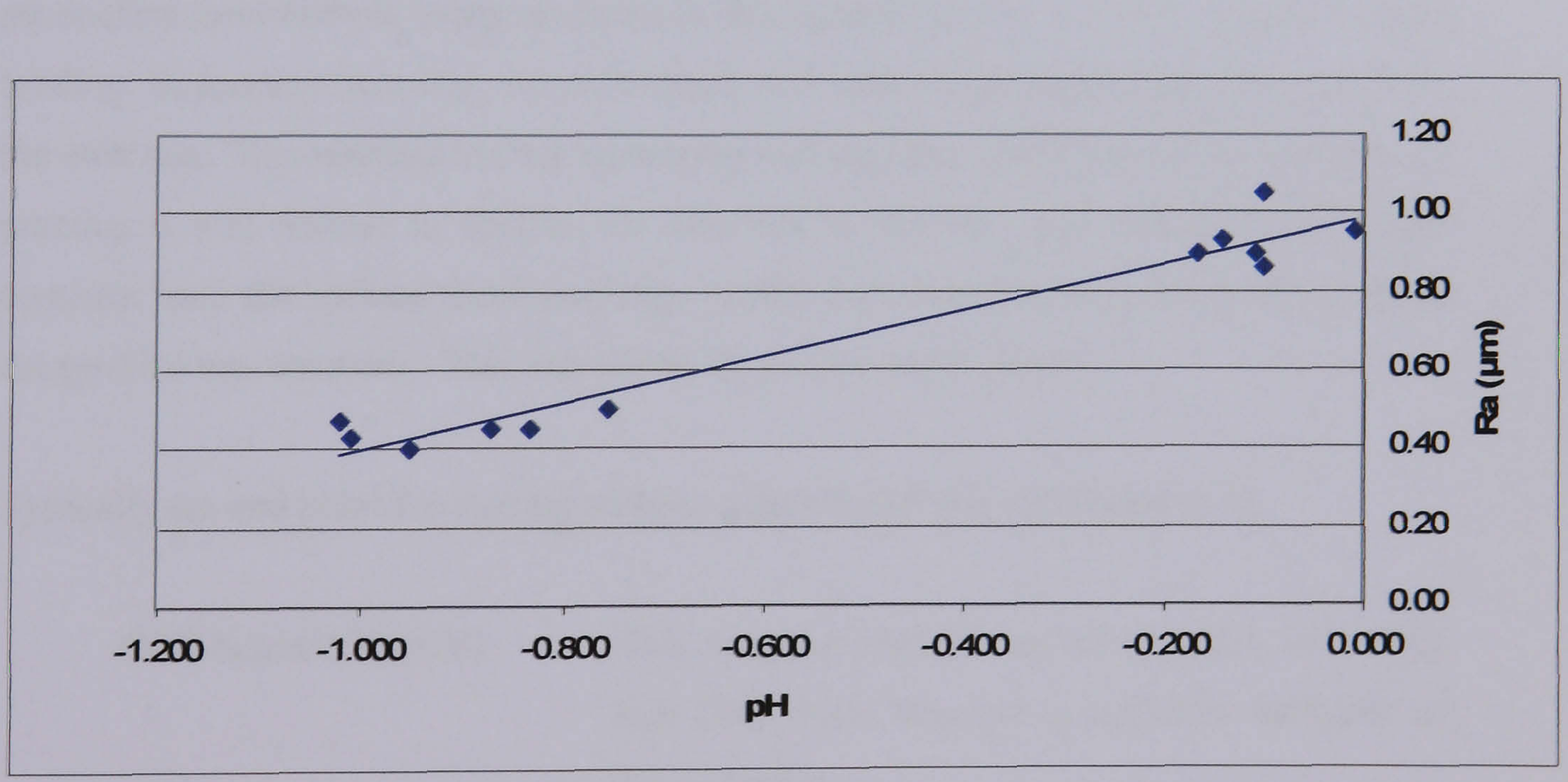


Figure 6.10 Typical surface finish for given pH showing results for the start and end of each base-line test. Note how the metal surface becomes increasing rough as the etchant is exhausted. (i.e. pH approaches 0)

6.2.2 Conclusions for base-line assessment

From the data recorded, and the analysis undertaken it is possible to determine an operating window at which the etchant should be used if productivity and product quality are to be maintained. It is also possible to estimate the 'end point' for etching with no form of regeneration.

The ideal operation parameters are:-

ORP between 600 and 590 (mV)

pH between -0.8 and -0.6

These should result in the following production parameters

Etch rate between 25 and 35 μm/min

Surface finish between 0.4 and 0.6 μm

Typically these parameters could only be maintained for a period of 1 or 2 days in the production environment being studied and this equated to a very small change in metal loading. In practice however, the etch speed was reduced to compensate for changes in the etch rate. This resulted in ever increasing etching times and reduced productivity. In practice it was normal to operate the machine in this way and typically this would continue until the surface finish and edge profile had deteriorated to the point at which the product was unusable. This was normally a 4 to 6 week period.

Typically the end point for etching without regeneration was concluded to be,

ORP below 530 (mV)	This varied across the tests conducted, indicating that ORP alone was not a sufficient indicator of the end point.
pH above -0.1	This was typical across all the tests and therefore indicated that this was a good measurement for determining the end point.

At this point the metal loading was only 15g/l. The average cost of etching at this level of metal loading was £18/kg . An analysis of the economics associated with etching without regeneration is given in Chapter 7.

6.3 BEAC test

6.3.1 Observations from BEAC tests

The results of the test are shown in summary in Figure 6.11. From this it can be seen that the BEAC system kept the ORP of the solution reasonably stable. The ORP fell from its initial point of 607mv to the set point of the equipment, 580mv. Dosing then took place and the additions kept the solution within acceptable limits. During this period the etch rate of the machine stayed within controlled limits as shown in Figure 6.12.

During week 7 of the test, both the ORP and the pH fell sharply. On investigation it was found that the probe that monitors the ORP had failed. Hence no additions had been made and no regeneration was taking place. Replacement of the probe overcame the problem and the solution regenerated back to the set point.

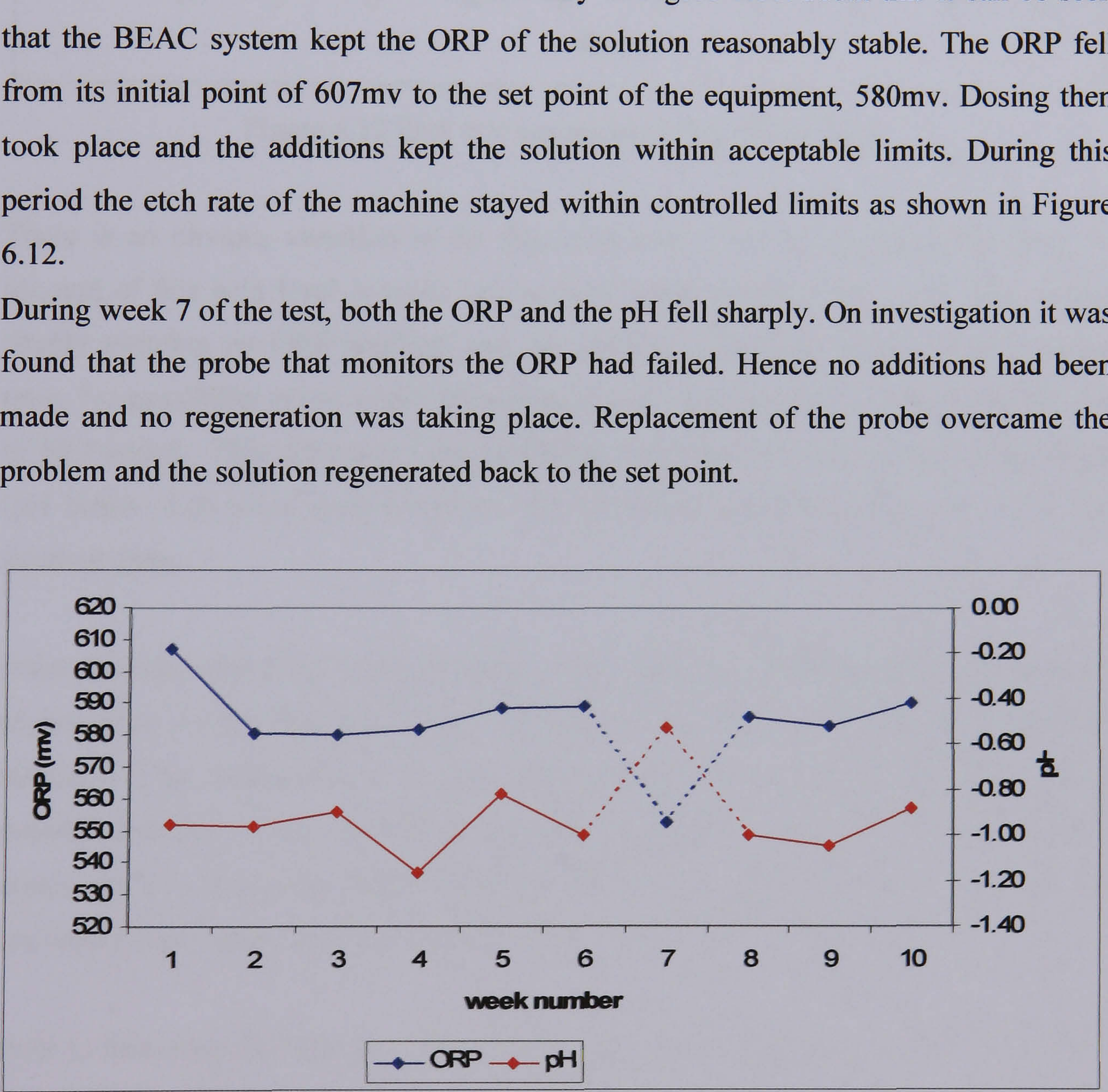


Figure 6.11 Results of 10 week BEAC test showing relationship ORP and pH readings

(testing stated on 11th Feb 2002)

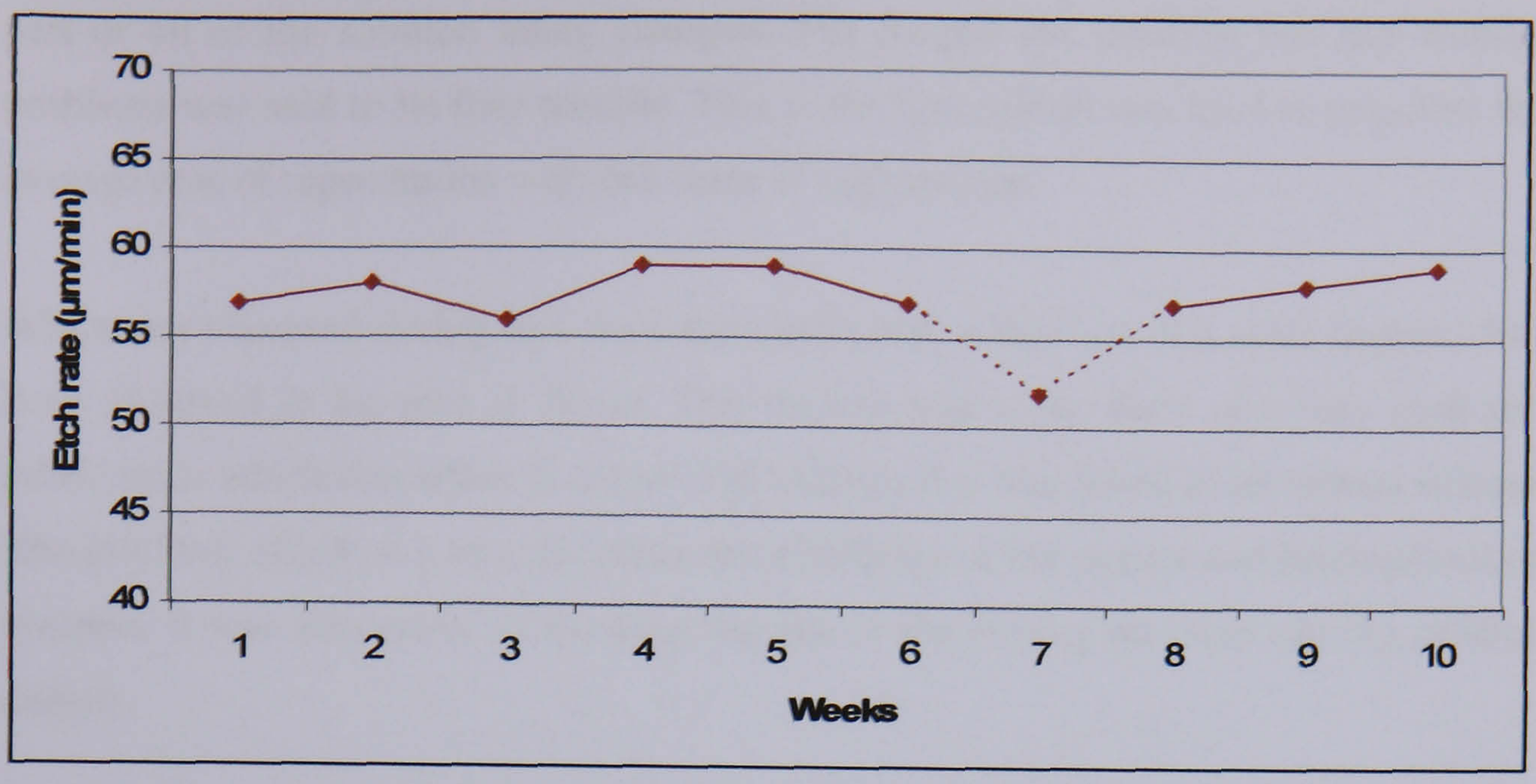


Figure 6.12 Etch rate variations during BEAC tests

There is an obvious variation in the free acid level. This is not surprising since no account of free acid level is taken into account when additions are made. The system simply switches on ORP readings and the additions which are made are of constant ratio. No possibility exists within the equipment to either monitor or adjust the amount of HCl added. This did cause some problems when the free acid level was very high (pH below -1.0) when some evidence of breakdown of the resist was noticed on the finished parts.

From the data recorded it was possible to calculate the cost of etching with this type of regeneration for the duration of the test period. This was £9.43 per kg of material removed. This represented a 52.6% saving on the cost without regeneration. It is possible that this saving could have increased slightly as the regeneration could have continued for a few more weeks. However, this part of the research was stopped after ten weeks due to other mechanical failures within the BEAC control system.

Prior to this controlled test run, this form of regeneration had been used for well over a year at Tecan. In discussion with Tecan staff it was found that similar problems had occurred in the past. Failures had occurred in both the pump system and valves which control the flow of chemical additions into the mixing chamber. Such failures inevitably lead to the solution becoming contaminated with excessive additions which resulted in

part or all of the solution being changed. The longest the machine had run without problems was said to be four months. This is the time which was used to calculate the average cost of regeneration with this form of regeneration.

Whilst not observed during this short time scale test, a build up of a scale deposits had been observed in the past at Tecan. This deposit was in the form of a very hard and brittle scale which was white in colour. On analysis this was found to be ferrous silicate. The practical effect of it was to reduce the efficiency of the pumps and heating/cooling systems. It was also prone to blocking the jets of the etching machine causing product defects.

Prior to these tests a probe had been installed to allow the conductivity of the solution to be monitored. Figure 6.13 shows the conductivity for the period of the test.

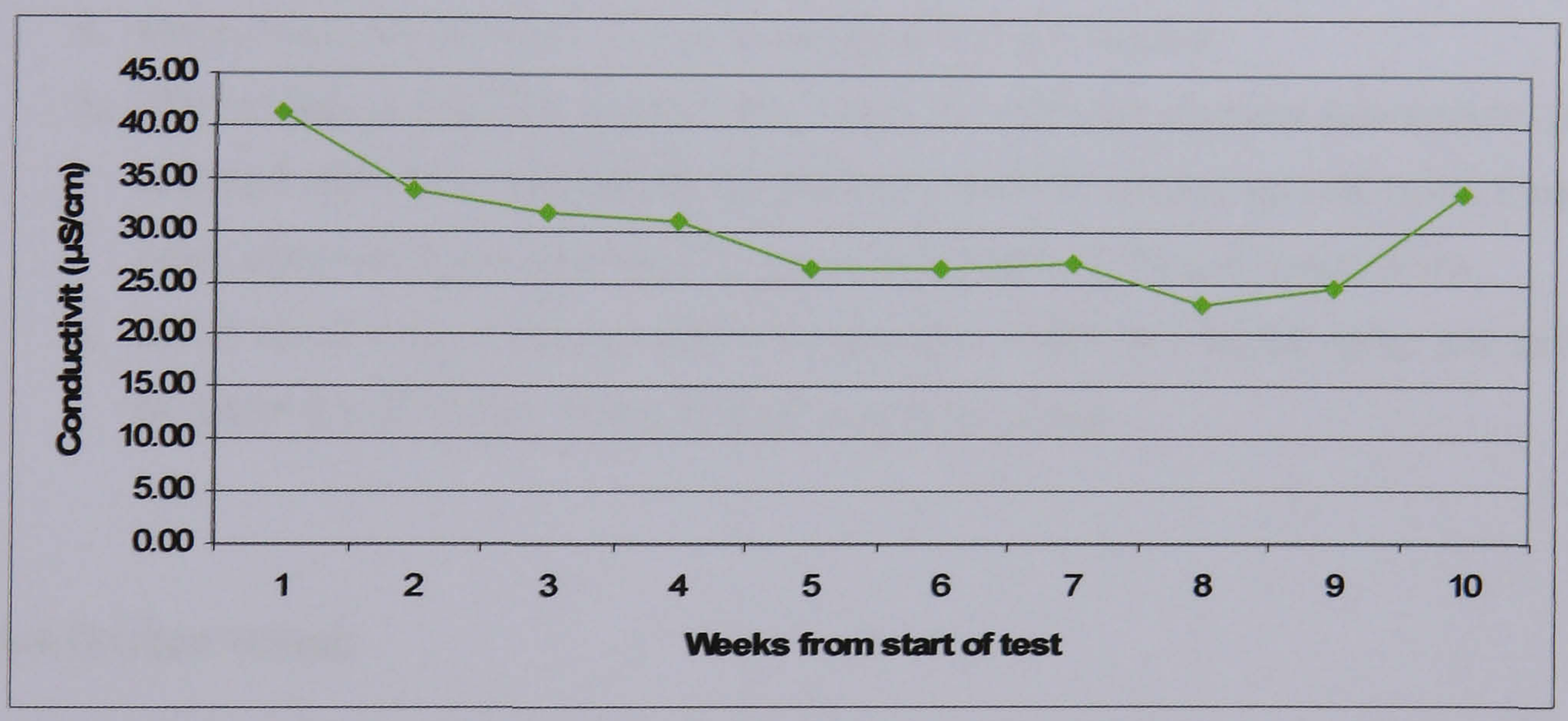


Figure 6.13 Chart showing change in conductivity during the 10 week BEAC test.

From this figure, it is concluded that conductivity on its own has little value in the monitoring of the solution. There would appear to be little, if any, correlation between the conductivity values and the pH. The pH is thought to be a more reliable indicator of the free acid level of the etchant. It is felt that the variation in conductivity results obtained could be accounted for by the build up in other elements within the etchant. It is fair to assume that the Fe^{2+} will not affect the reading since this is being regenerated.

The ORP results would support this. However, the Ni^{2+} and Cr^{3+} would not be regenerated by this system so would complicate the reading.

6.3.2 Conclusions from BEAC test

From the work undertaken, and discussions and analysis of previous use of this form of regeneration, the following conclusions have been drawn.

1. The estimated cost of regeneration using the BEAC system is £7.82/kg
2. The metal loading of the solution had increased to 49g/l of solution used, a 327% increase over the test with no regeneration.
3. It is essential that good maintenance is performed at regular intervals to prevent equipment failure which in turn can lead to contaminated etchant
4. On average, the solution will need changing every 4 months
5. The system is relatively easy to use. Once set, minimal operator intervention is required other than keeping the additional chemistry topped up and monitoring other parameters not controlled by the system, such as SG and temperature.
6. Build up of a hard silicate deposit is possible which will block spray jets and decrease the efficiency of heating and cooling systems.

6.4 Oxygen testing

6.4.1 Introduction to Oxygen experimental work

The practical research with oxygen formed the bulk of the experimental work undertaken during this study and was carried out over a period exceeding three years. To detail all the experiments undertaken would be impractical and this section aims to give an overview of the work. It has been divided into five main experimental groups.

- **Verification of work carried out during previous research and as described in** IBM patent (Lubert et. al. 1993)
- Experiments with various flow rates of oxygen and HCl.
- Extended time scale experiments carried out overnight.
- Tests conducted with the static mixer operation vertically.
- Prolonged testing with controlled free acid levels.

During the experimental work, specific gravity of the etchant was controlled by manual additions of water; the aim being to maintain the Baumé of the etchant between 39° and 41°. The tendency was for the specific gravity of the solution to rise as water was lost due to evaporation. It was essential to maintain this level of control since specific gravity has a considerable effect on the etch speed.

6.4.2 Experiments conducted to verify and review previous research.

Initial experimental work started in 2003, with equipment construction and testing. The detailed experimental work started on 22nd March 2004 when the etching machine was filled with fresh ferric chloride etchant. Production was carried out in the normal way. As expected, the ORP of the solution decreased, on day 11 it had fallen from 590mV to 560mV. The oxygen regeneration equipment was turned on. The flow rates of both oxygen and HCl were the same as had previously been used by Peters [1999], (oxygen flow rate 4 litres/min and HCl at 25ml/min). The only change made was to the injection system. The HCl was now being injected immediately prior to the mixer. Additions continued for 4 hours whilst production was still running. At the end of this, the equipment was turned off as no change was seen in either the ORP or pH. This procedure was repeated over several days. No significant change in the acid condition was observed during any of these tests. By this point the surface finish and etch speed had fallen further, the ORP dropping to 578mV. In order to maintain the output of product it was decided to cease the experimental work. 200 litres of ferric chloride was pumped out of the machine and replaced with fresh etchant. This had the obvious effect of increasing ORP and production was restarted. It was felt that one reason that regeneration was not occurring could be the fact that only limited amounts of metal

were being etched into solution. This would have resulted in low levels of Fe^{2+} being available for regeneration. In an attempt to verify this, on several occasions complete blanks of metal were dissolved, adding some 6Kg to the amount of metal already in solution. The aim was to drop the ORP significantly and hence increase the amount of ferrous material in solution. The result of this was a drop in ORP by some 15 mV but during regeneration no corresponding increase was seen. Testing continued in this way for 3 months.

At this point it was decided to significantly increase the flow rates of oxygen and HCl. The old etchant was removed and the machine cleaned.

6.4.3 Experiments with various flow rates of oxygen and HCl.

Starting with fresh etchant on the 10th May 2004, production was started and the ORP was allowed to fall as in the previous test. During the following weeks a series of tests using various flow rates of HCl and oxygen were carried out. Tests were conducted with flow rates in the ratio calculated from the regeneration equations and variations in the proportions of each. Air was also used in place of the oxygen during some of these tests.

During one of these tests, when the flow rate of oxygen was 25l/min, it was noted that oxygen was seen bubbling out of the exit point from the mixing loop into the sump of the machine. Prior to these tests the mixing loop had been modified to add an extra length of static pipe prior to return to the sump as the literature search had indicated that this was a potential weakness in the previous design. But it was clear from this observation that not all of the oxygen present was being combined with the ferrous chloride within the etching solution to initiate regeneration. It was extremely likely that same or all oxygen would have been 'lost' in this way during previous research.

As with the previous test, no significant change was observed in the etchant condition as a result of the regeneration attempts and the tests were stopped after two months.

No definite explanation could be found for the different results obtained from these tests compared with previous research. The only difference between the experiments was the position at which the HCl was injected. It was felt possible that the actual free acid levels in the previous research could have been significantly higher than those reported since the HCl was injected directly into the sump of the machine and the sampling and control loop was only fed by a low flow rate pump. This would also have had the effect of dropping the ORP value. It could also be an indicator to higher free acid levels being required to initiate regeneration. In general these tests had been conducted with pH in the region of -0.2.

6.4.4 Extended time scale experiments carried out overnight.

Since the presence of high free acid levels appeared to be significant and the static mixer did not appear to be having any significant effect on the regeneration process it was decided to conduct experiments using only HCl additions. The addition of oxygen would be provided by the spray jets within the etching chamber of the machine. Oxygen was present in the machine in the form of air, which naturally contains 21% oxygen.

The etching machine being used for the research work had 224 jets in total, arranged above and below the conveyor that carries the work being etched. This is shown in Figure 6.14. The theory was that these sprays formed tens of thousands of tiny droplets of etchant as the etchant was forced at pressure out of the spray heads. It was felt highly likely that there was more potential for absorption of oxygen in this method compared with the static mixer since the available contact area was significantly greater. Contact time is one of the critical factors which determine the effectiveness of gas absorption in a liquid [Siddey 2005 and Sulzer 2005]. In practice this was found to be the case and this form of combining the oxygen (from air) with the etechant was extremely effective. It also offers significant cost savings in terms of equipment and chemical costs. The control system was used to maintain the pH of the etchant at predetermined set points, additions of HCl being made as required.

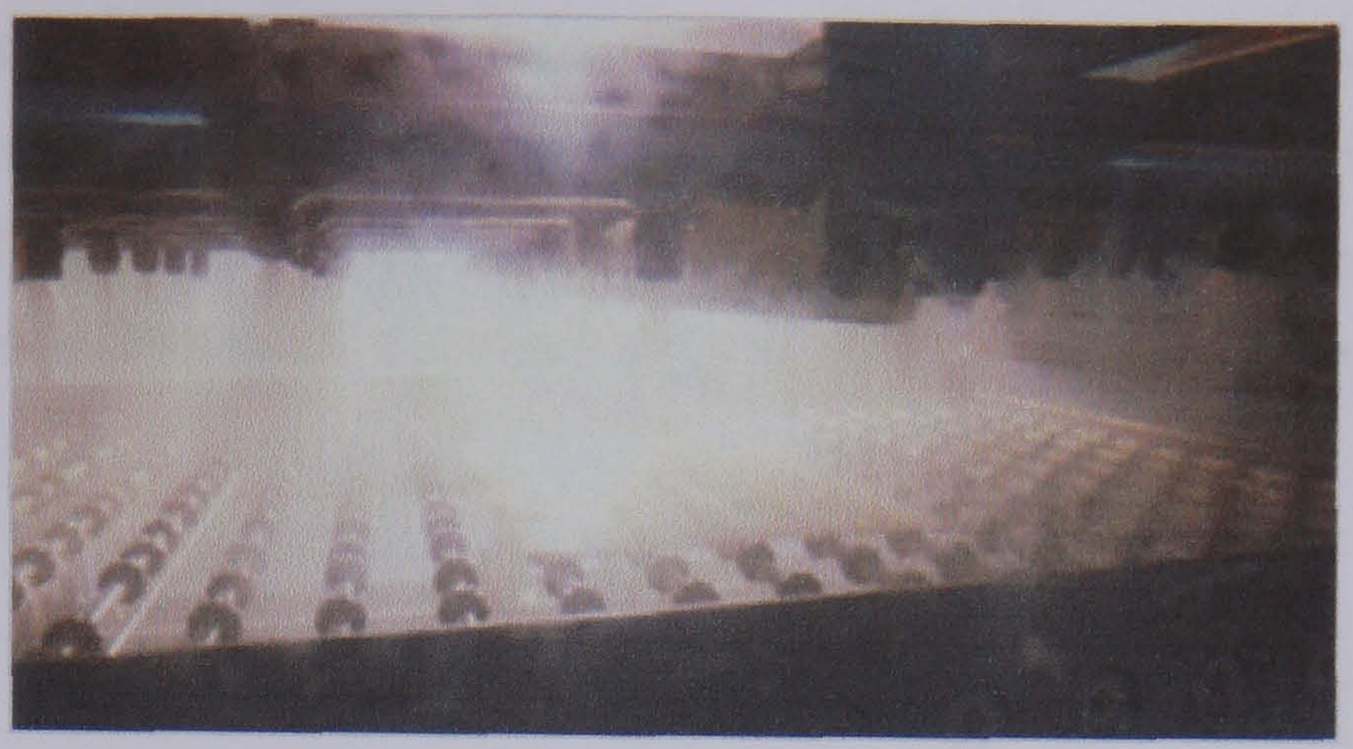


Figure 6.14 Inside of etching machine showing spray jets

The first test was conducted on the 6th September 2004. The result of this is given in Figure 6.15. From this it can clearly be seen that the ORP increased during the period of the test. Additions of HCl were made to maintain the set point of -0.5. During this test only a limited amount of production work was being processed. The effect of etching production work is seen particularly around 11:30, when the pH rises.

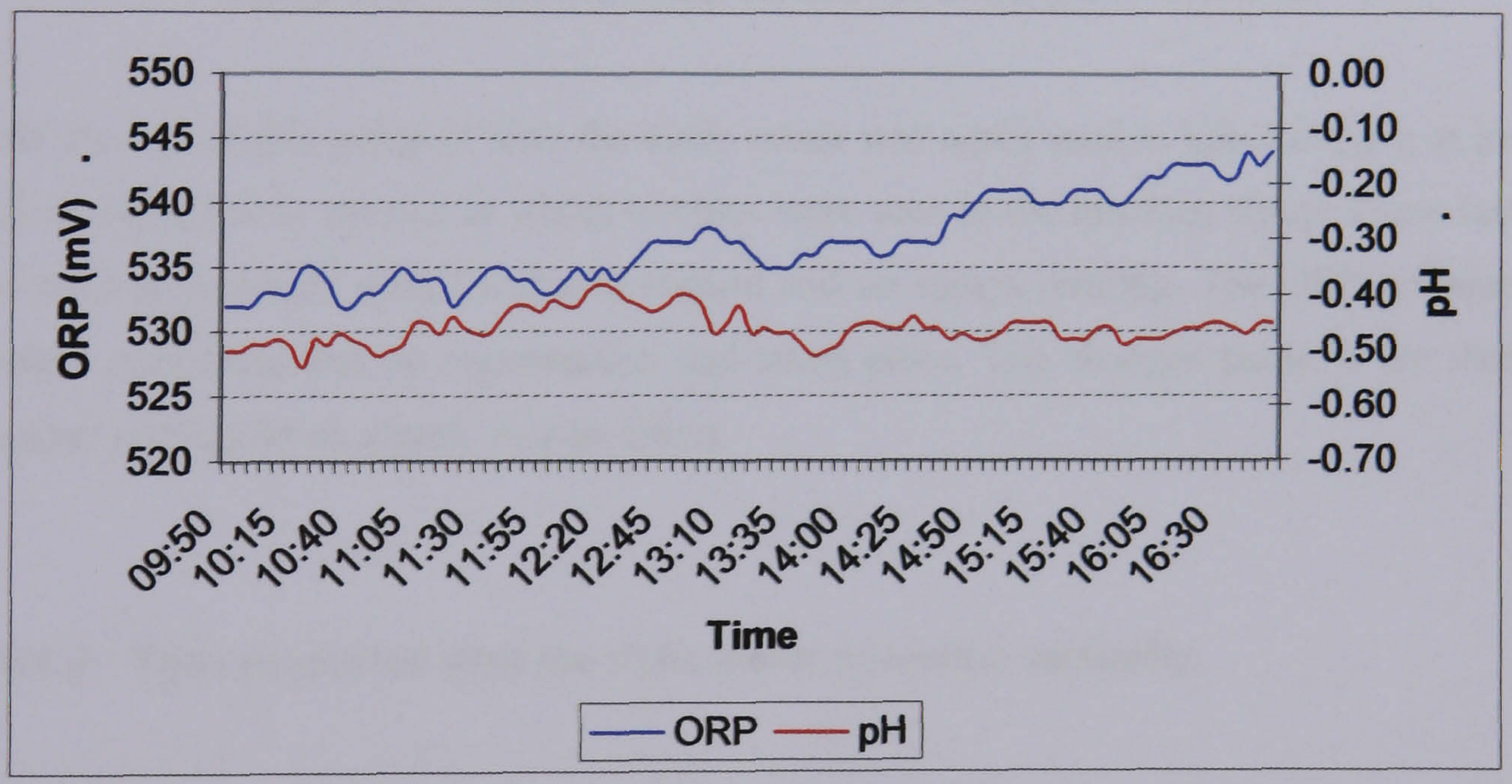


Figure 6.15 Results of test carried out on 6/9/04

During the following months a series of tests were conducted overnight. It was considered essential to conduct these experiments when no production work was being processed in order to obtain an accurate understanding of the reactions taking place

which could otherwise have been masked by changes in the etchant due to the additions of the dissolved metals. Figure 6.16 shows a typical result of these experiments. The pH has been held at the lower set point and the ORP increased, indicating that some regeneration of the ferrous chloride back to ferric chloride has taken place.

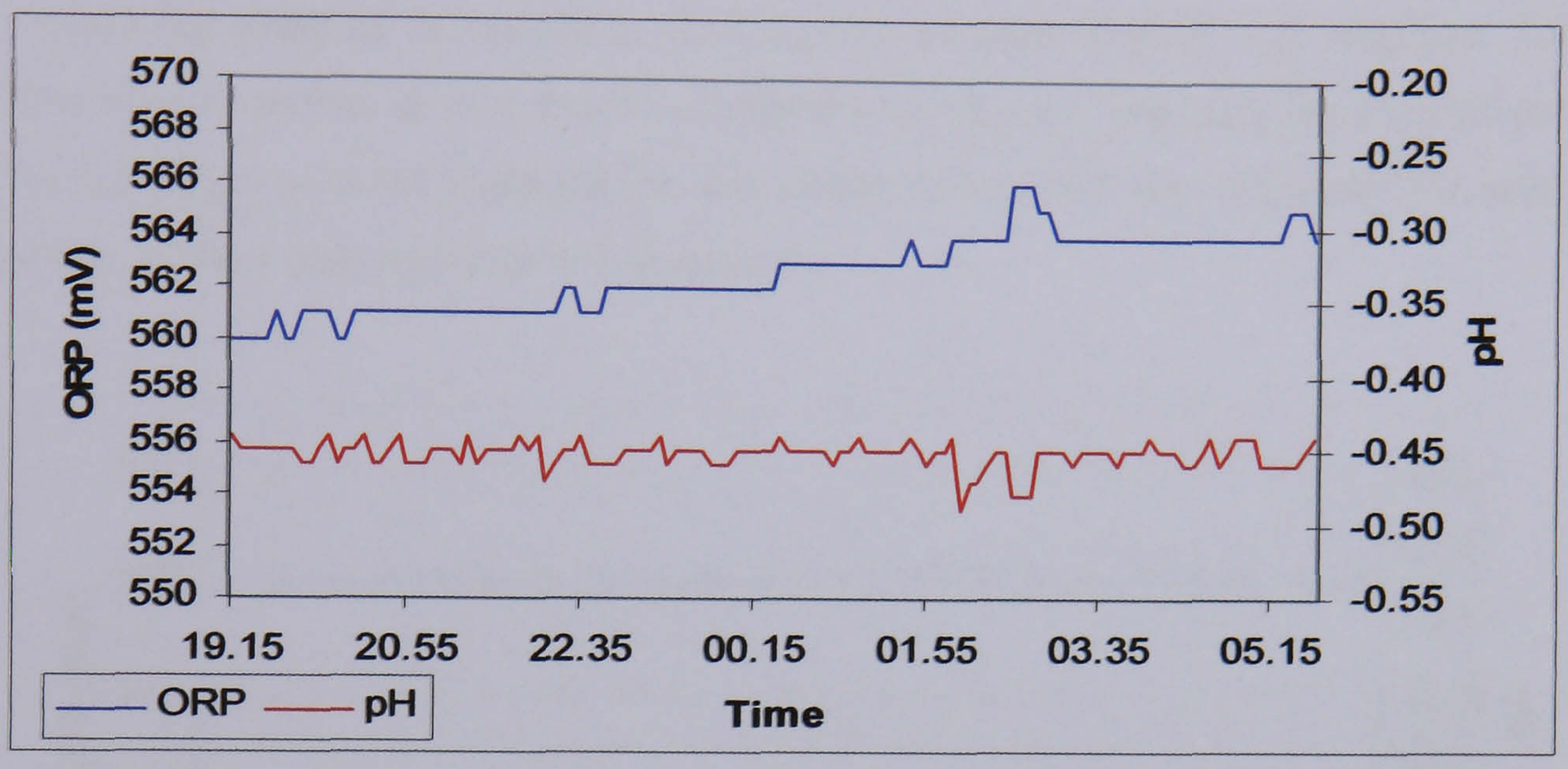


Figure 6.16 Results of test carried out overnight 6th Oct 2004

At the end of this series of tests the static mixer was again used to inject oxygen at low flow rates, below the rate at which bubbles were seen in the machine sump. These tests were run overnight with fixed acid control and no sprays running. The ORP remained static indicating that no regeneration had taken place. The changes made to the static mixer configuration clearly had no effect.

6.4.5 Tests conducted with the static mixer operation vertically.

Following detailed investigation of the use of static mixers it was decided that it would be worth conducting a series of short experiments with the mixer configured in a vertical rather than a horizontal mode. The aim was to improve the potential for oxygen to be absorbed into the etchant by prolonged contact times between the two reactants. The equipment was modified accordingly (Chapter 4).

Using the etchant from the previous experiment, tests were conducted with both oxygen and compressed air being pumped into the mixer. The free acid level of the machine was maintained at a constant level of -0.5. With low flow rates, below 10 l/min, absorption was improved and no bubbles were seen where the static mixer return pipe entered the sump of the machine. However no increase in ORP was observed. With flow rates in excess of this, bubbles could clearly be seen indicating the absorption of the air/oxygen was not complete. No movement of the ORP was observed. The results of one of these tests is shown in Figure 6.17

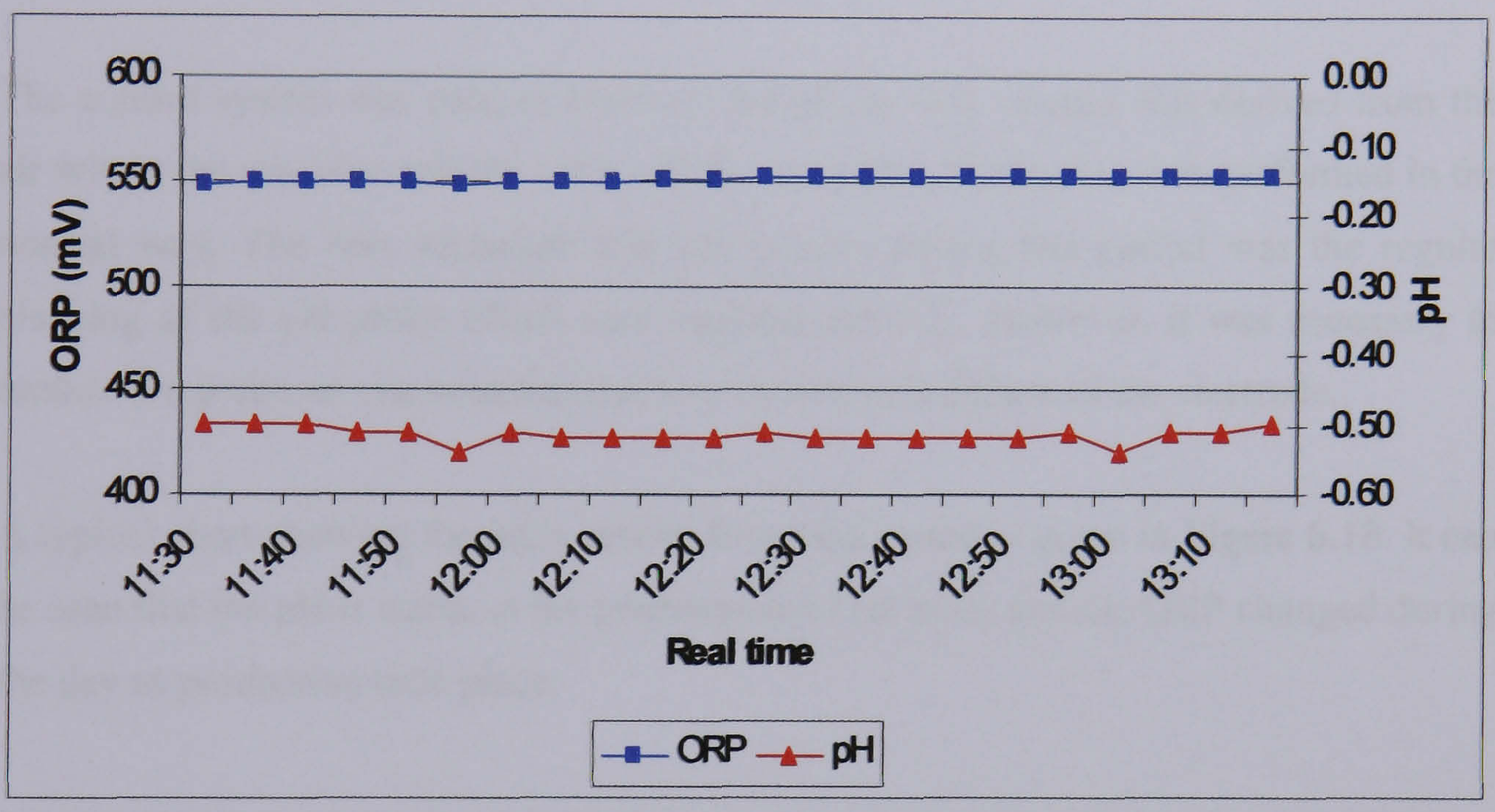


Figure 6.17 Results on typical test with static mixer running in vertical mode

(from test run 11 3 2005)

Time did not permit extensive testing at this stage; it is possible that modifications to the static mixer configuration or the addition of additional mixing stages could have resulted in better absorption. However the results obtained without the mixer were proving very interesting and it was decided to continue with this work in preference to modifying the mixer circuit further.

6.4.6 Prolonged testing with controlled free acid levels.

The earlier experimental work had shown that the free acid level was critical and the use of the static mixer was having limited, if any, benefit to the process. It was decided to conclude the experimental work with a prolonged experiment. The objective was to see if the machine could be run for a period with minimal technical intervention whilst maintaining product quality and production speed. The test was started in January 2005 and the machine was emptied and cleaned. The previous etchant was reused and a small amount of fresh ferric chloride was added to bring the machine to the operating level. The test ran until November 2005.

The control system was used to maintain the pH at -0.6, oxygen was derived from the air within the machine and the action of the spray jets. Production was performed in the normal way. The only technical task carried out during this period was the regular cleaning of the pH probe which was required monthly. However, it was necessary to replace the probe on one occasion due to a catastrophic failure of the electrode.

A typical chart showing the daily results from this period is given in Figure 6.18. It can be seen that the pH is stable at the predetermined set point and the ORP changed during the day as production took place.

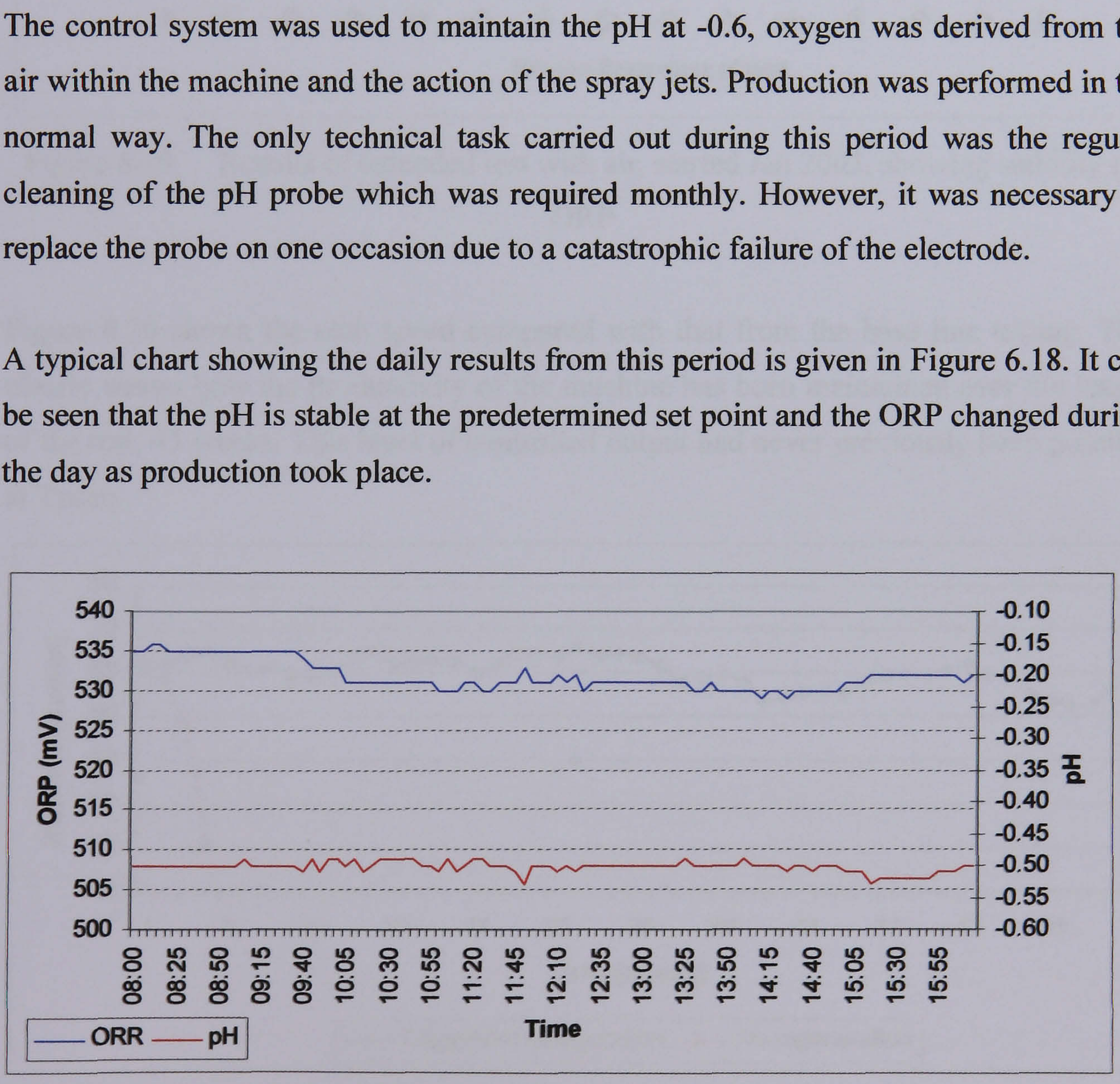


Figure 6.18 Typical ORP and pH chart from the end of the oxygen/air regeneration test.

(results from 4/5/05)

Of more significance is the chart shown in Figure 6.19 which plots the ORP over the entire length of the test. This shows the average ORP for each week of the test and indicates the level of stability which was achieved.

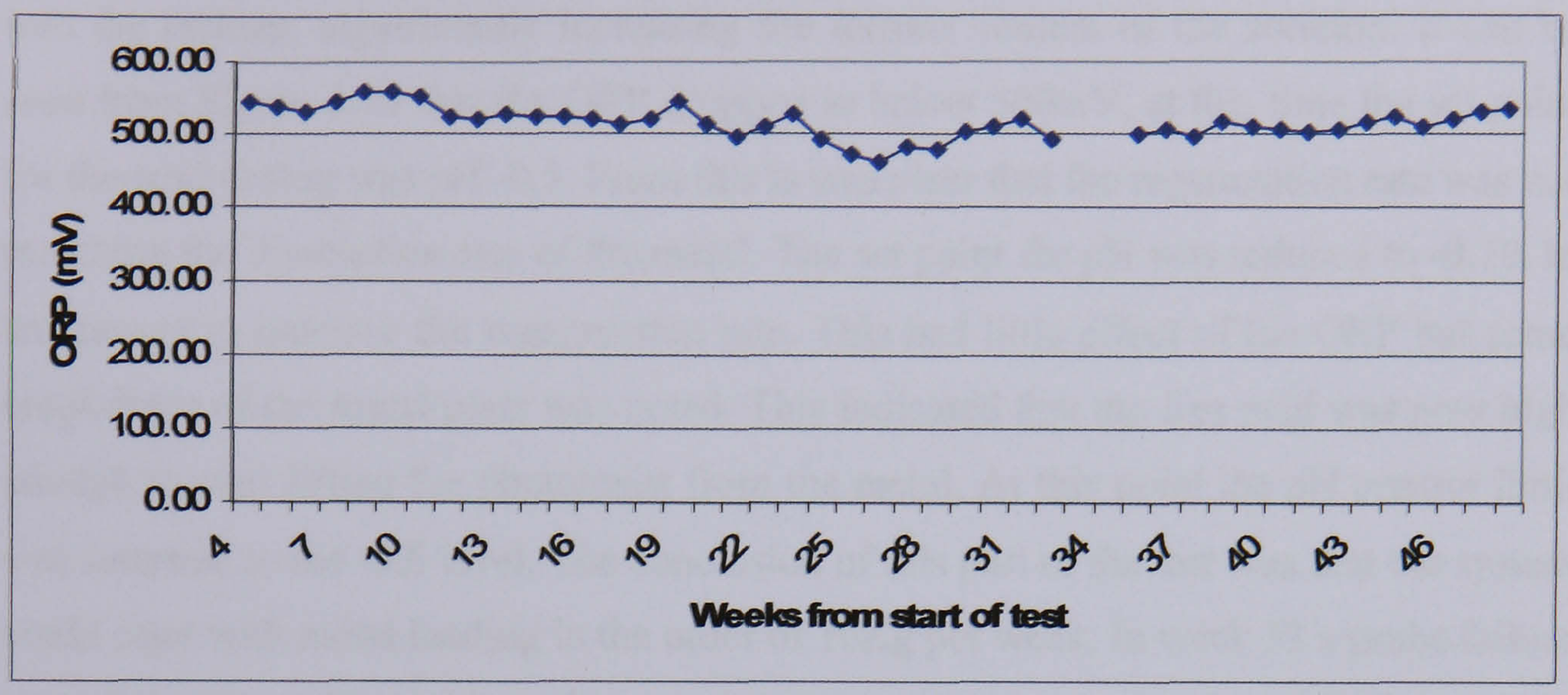


Figure 6.19 Results of extended test with air, started Jan 2005, showing stability of ORP

Figure 6.20 shows the etch speed compared with that from the base line testing. This clearly shows how the productivity of the machine has been maintained over the length of the test, 45 weeks. This level of controlled output had never previously been possible at Tecan.

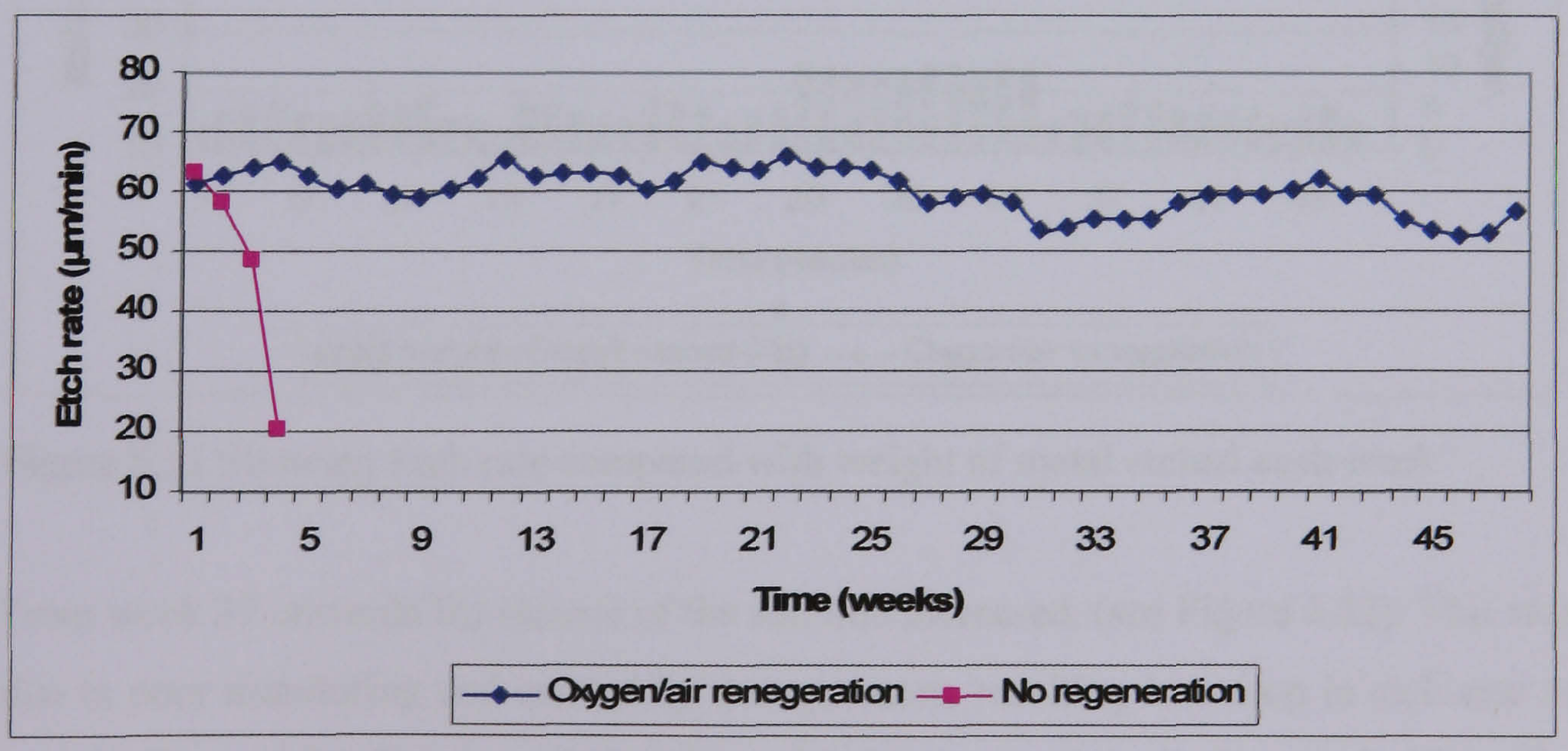


Figure 6.20 Results of extended test, started Jan 2005, showing stability of etching speed.

During weeks 25 to 33 of this test additional metal was dissolved into solution. The aim was to see if the regeneration system could maintain the OPR at the desired level with increased metal loading. Each day a sheet of stainless steel was completely dissolved into the etchant, significantly increasing the ferrous content of the solution. It can be seen from Figure 6.19 that the ORP dropped to below 500mV, at this time the set point for the acid dosing was pH -0.5. From this is was clear that the regeneration rate was not matching the dissolution rate of the metal. The set point for pH was reduced to -0.70. in an attempt to increase the regeneration rate. This had little effect of the ORP but some breakdown of the metal parts was noted. This indicated that the free acid was now high enough to start lifting the photoresist from the metal. At this point the pH control limit was returned to the -0.6 level. The conclusion of this part of the test was that the system could cope with metal loading in the order of 10Kg per week. In week 33 a probe failure caused the free acid level to reduce to -1.2. It was necessary to replace 200 litres of the etchant with fresh ferric chloride in order to maintain production.

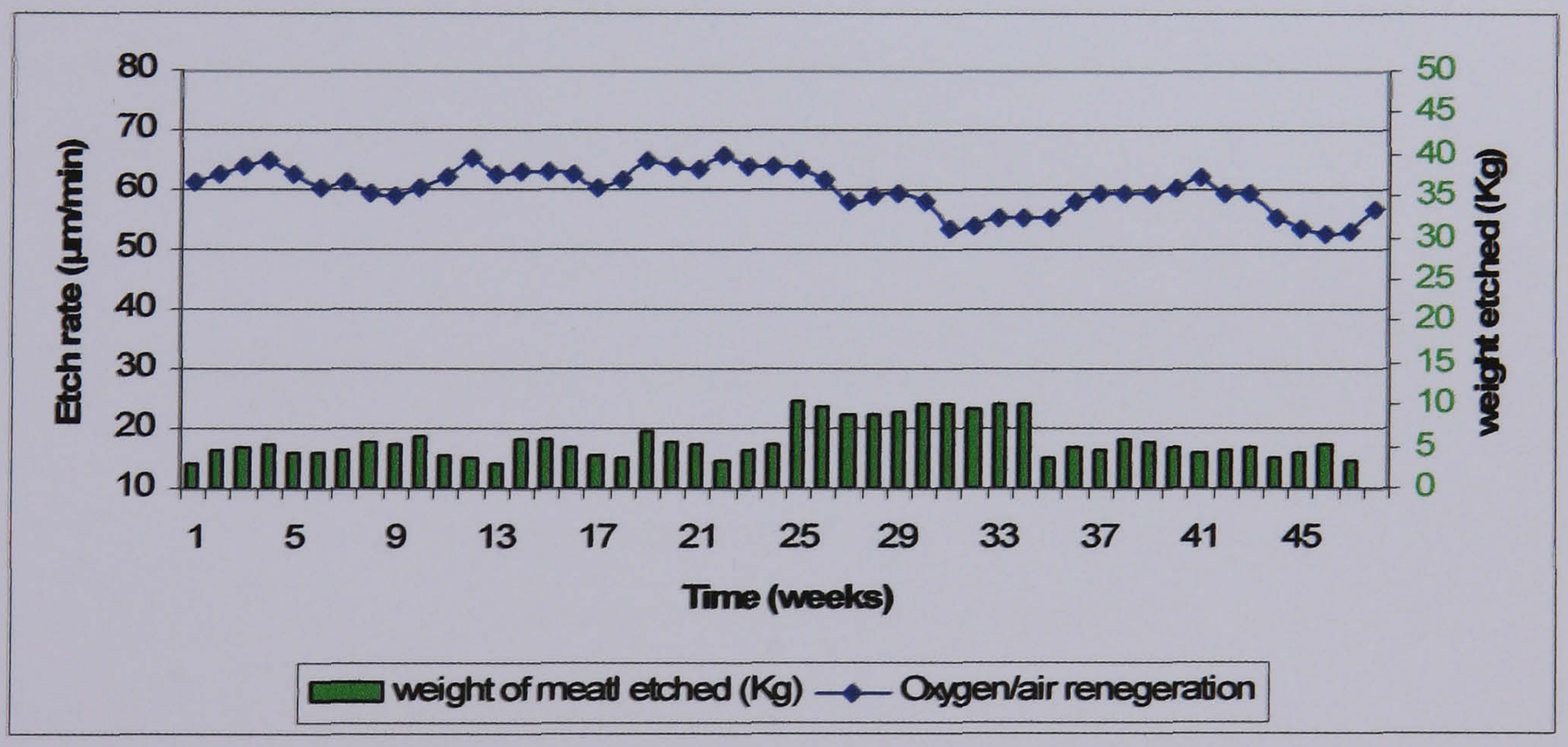


Figure 6.21 Showing Etch rate compared with weight of metal etched each week

From week 37 onwards the Baumé of the solution increased, (see Figure 6.22). This was due to poor monitoring and control by the operators, resulting in a drop in etch rate as seen in Figure 6.21. This is entirely inline with the theory given in Chapter 3. When the

Baumé of the solution was lowered the etch speed began to rise. Charts relating to this are given in Appendix 16

Conductivity was measured during all of these tests in order to verify the conclusion from the earlier testing. This being that conductivity measurement was unreliable for determining the value of free acid. The results of these measurements are given in Appendix 16. The conclusion is that conductivity varied widely in relation to pH and is therefore not considered as a reliable method of determining free acid in anything other than virgin ferric chloride etchant. This is probably due to the build up of conductive elements (Ni^{2+} and Cr^{3+}) within the etchant over time.

7.0 Discussion and Recommendations for Further Work

7.1 Introduction

From the analysis of the considerable amount of data gathered during this research a far greater understanding regarding the nature of ferric chloride consumption during the PCM process was gained. A great deal of knowledge has also been built up regarding the methods which can be employed for monitoring and recording what was previously thought of as a complex and difficult-to-predict production system. As a result, a simple monitoring system has been developed and deployed. Whilst the oxygen regeneration was not successful in the form originally and previously studied, the alternative system developed is practical, better controlled and economically viable. This allowed the constant use of etchant for a period of 18 months, which prior to this research would have been replaced every 16 weeks. For the largest part of this period the regeneration has been possible using only air and small quantities of HCl, by far the most environmentally friendly process available. Whilst these economic results can only be considered correct for this particular manufacturing situation, which involved relatively low dissolved metal concentrations, many of the benefits and observations drawn from this work will benefit the general PCM industry.

The following sections detail the discussion in 5 areas:-

- Monitoring and control systems
- Importance of free acid and automation
- Commercial evaluation
- Product quality, productivity and eradication of scale build up
- Environmental and safety impacts

7.2 Monitoring and control systems

This study has concluded that it is both feasible and practical to monitor the etchant used in the PCM process in 'real time', remotely across a standard business network. The level and complexity of the systems used in this study are certainly more elaborate than would be required in a production situation. This was however necessary in order to obtain the amount and detail of data required of this study. A simplified system is described in section 7.7.

To accurately determine the condition of the etchant it is suggested that ORP and pH are measured. From the results of the baseline assessment it is concluded that ORP is a very good indicator of the level of Fe^{2+} in solution. This is clearly seen in Figures 6.3, 4.4 and 6.6 with the ORP falling as metal is dissolved into the etchant. Whilst this is the result which was expected the fact that this has now been confirmed in a production environment over a long period of time with such ease is a clear indicator of the value of ORP measurement. However, ORP alone is an insufficient indicator of the etchants full condition. As was seen in the base line tests the end point ORP reading varied significantly. It is therefore considered essential that the free acid levels must also be determined if a full understanding of the etchant is to be obtained. The best method of determining free acid is considered to be the measurement of pH. It is felt that this is far superior to conductivity and titration; this is discussed further in section 7.3

Most commercial regeneration systems rely solely on ORP measurement. This could lead to production problems if the free acid levels are allowed to change significantly due to incorrect additions of regeneration chemistry.

It is felt that such monitoring should be installed as a matter of course in PCM etching facilities. The cost is not prohibitive (in the region of £3k) and the benefits achieved are considerable. These include:-

- Improved accuracy of loading of production on the machines dependant on the acid condition. In normal operation the machine would be loaded with metals in a particular sequence according to the condition of the acid. i.e. stainless steel first, then the copper-based alloys followed by aluminium-based alloys. Such controls would improve both product quality and productivity. It also increases the utilisation of the etchant.
- Machine defects can be seen. Proactive rather than reactive control becoming a real possibility. The study clearly showed when machine defects such as worn anti-contamination rollers or water leaks occurred. Such defects were detected quickly by unexpected changes in the etchant chemistry which, without monitoring, would have continued until the etchant was affected to such an extent that defective products could have been produced.
- The monitoring can be used to send alarm signals, possibly in the form of emails or SMS messages to supervisory personnel if critical control factors were breached.
- Accurate additions of chemicals can be made at the optimum time and in a controlled way. If manual analysis is carried out it will inevitably lead to delays in making the additions, during this period the etchant will have changed. Therefore any additions made as a result of manual analysis would probably be of incorrect amounts.

7.3 Importance of free acid and automation

Clearly the control of the free acid is critical to this form of regeneration. It is believed that the presence of free acid performs two important functions.

1. By keeping the free acid level high, the dissolved metals are kept in solution, reducing the possibility of forming metal hydroxides which would precipitate out and affect product quality due to blocking of spray jets and pipes. This is particularly important for the Ni and Cr elements which are not regenerated.

2. It acts as a source of chlorine. The chloride ions act as a sink for the oxygen (present in the air) thus allowing regeneration to take place according to the formula, $3FeCl_2 + 3HCl + 3/4O_2 \rightarrow 3FeCl_3 + 3/2H_2O$

From this research it is considered that the free acid of the solution should be maintained between pH -0.5 and -1.0. Lower than -1.0 it is extremely likely that the product quality would suffer due to resist breakdown. If the etchant has a pH value higher than -0.5 it is likely that there would be insufficient free acid present to keep the dissolved metals in solution and act as a chlorine sink to facilitate regeneration.

It is concluded that pH measurement is the most suitable for this control. The use of conductivity is only suitable for free acid measurement within virgin etchant due to the variation in the results when etchant containing dissolved metals is measured. These variations being caused by the build up of those metal ions that are not regenerated such as chrome and nickel.

The system developed simply pumps HCl into the etchant at a controlled rate. This was easily controlled by monitoring the pH of the etchant and using this to switch the pump on and off. No 'off line' analysis is required which would add cost and delay to the process. The latter point is especially relevant since in production the delays caused by the time taken to undertake manual titrations are considerable. Since the etching process would still be running during this analysis the results would inevitably be inaccurate due to the time delay. The effect of this would be to make additions which may not be the actual amount required.

This system is far simpler in both design and operation than those described in Chapter 2, commonly used in industry, even in low dissolved metal production facilities.

In the long term, it is likely that the etchant will need to be replaced. Since the build up of metal contaminants, such as Ni and Cr, would get to such a point that they will begin to affect the product quality and/or speed. Whilst this was not noticed during

this research, the literature suggests that this is the case for nickel [Allen, Almond and Maynard 2004]. At the end of the extended period of testing, the etchant had changed in colour considerably. It was no longer the dark golden brown colour associated with fresh ferric chloride but had become a dark brown/green due to increases in the concentrations of chrome and nickel.

7.4 Commercial evaluation

One of the major drives in any commercial enterprise is to reduce product cost; this must however never be at the expense of product quality.

As a result of the work undertaken during this study the cost of operating the etching machine used to produce stencil blanks has reduced considerably. At the start of the study the cost was £18.83/Kg. This was reduced during the early stages of the work due to small machine repairs and by minor modification to the operation of the machine. These problems were only noticed as a result of the monitoring carried out. The average cost without regeneration was calculated as £17.91/Kg. The work carried out during the BEAC study showed that the cost using this type of regeneration was £7.82/Kg. This figure compares very favourably with that theoretically predicted by the economic model described in Chapter 2. Any small deviations in the results were explained by variations in the amount of chemistry used and the difference in the assumptions used in the model compared with those present in practice. These include such factors as the cost of energy used, disposal costs and the financial equations used to calculate depreciation.

As a result of experimental work undertaken during this research the cost of etching with oxygen/air regeneration was to £2.97/Kg. this represents a 83% saving over the no-regenerated system.

A summary of the financial information is given in Figure 7.1. The true saving is likely to be higher. Management time, and hence cost, is reduced since improvements in process control result in less rejects etc. With further reductions in chemical cost, and the introduction of some of the additional enhancements detailed in section 7.7 more savings could undoubtedly be achieved.

Based on the standard investment calculations used by Tecan, this saving represents a saving of some £7,228 per year. Full details of the breakdown of these calculations are given in Appendix 15.

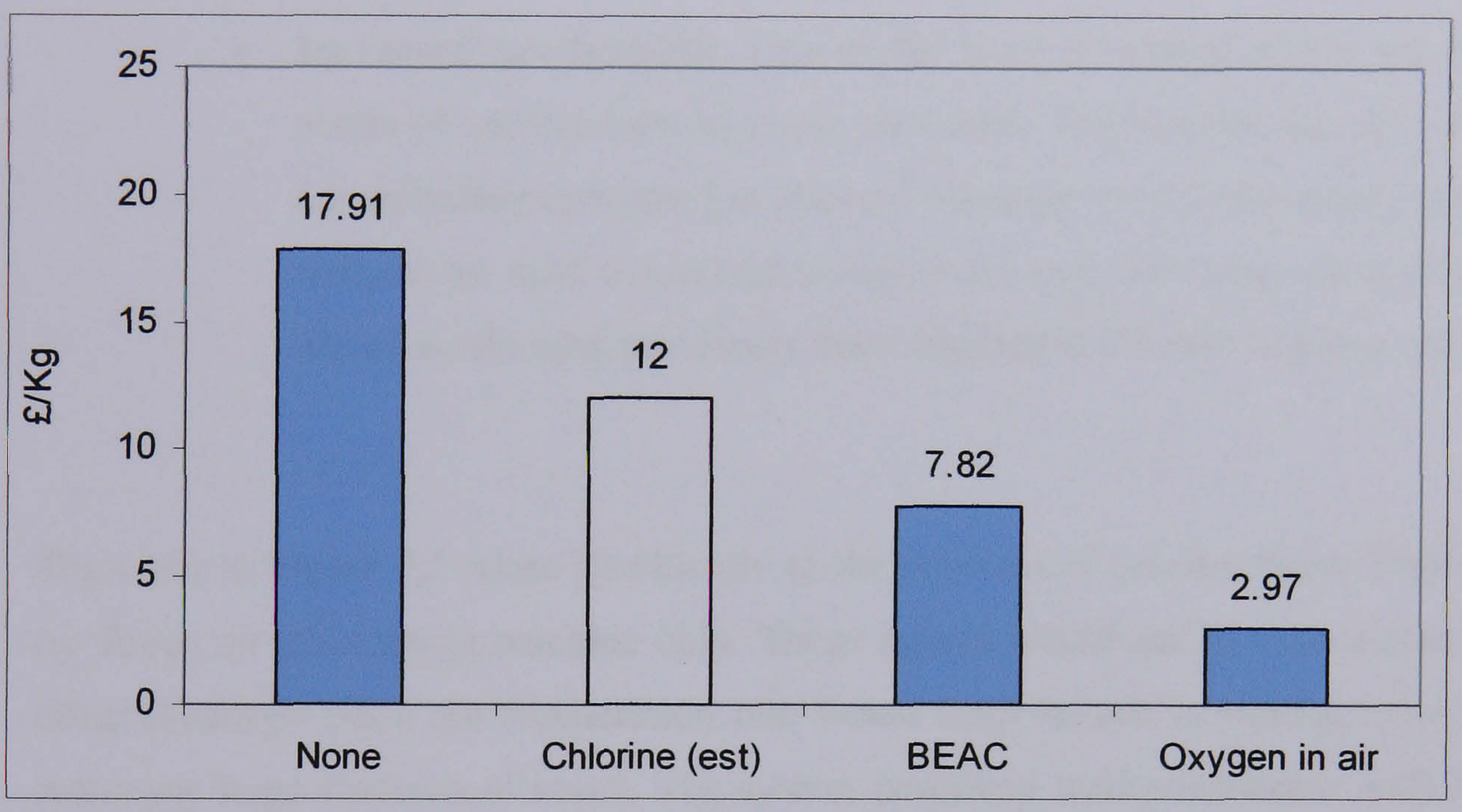


Figure 7.1 Comparison of costs for various regeneration systems. Assuming a metal removal rate of 500kg pa *(based on actual data, except for chlorine which has been estimated from the financial model)*

This significant saving has been achieved with very simple equipment, compared with the systems described in Chapter 2. It required little management or maintenance and could easily be incorporated into any existing etching machine. The cost saving obtained can be accounted for in 4 areas:-

- **Reduction in chemicals used**. The regeneration process obviously eliminates the need to replace the ferric chloride every few weeks as

was the case when no regeneration was used. The use of air in the place of pure oxygen also has obvious cost advantages, using the sprays within the machine even eliminates the cost of compressing and delivering the air.

- **Reduction in chemical disposal.** Since no new ferric chloride is used no waste ferric is produced which requires controlled disposal. Current disposal costs are £0.45/ltr.
- **Reduced labour.** To change an etching machine requires approximately 4 man-hours of work. This cost is completely eliminated.
- **Increased productivity**. Due to the level of control which has been achieved, productivity has been increased. The fact that the etch speed has remained constant has allowed operators to process work quickly without the need to test and calculate the etch rate using set-up sheets. These would have previously been required at the start of every shift.

The costs in Figure 7.1 relate specifically to the volumes of product being produced by Tecan on this etching machine only. These figures would not transfer directly to other situations since the regeneration rate would limit its use in etching machines removing large volumes of metal. The system described works extremely well with etch rates up to 500kg per year above this figure and some reduction in the ORP was noticed suggesting that the regeneration rate was not keeping pace with the etching rate. However when the etch rate returned to the lower level the solution ORP did return to the previous level after several days. It is felt that this could however be improved with increased oxidisation of the etchant, possibly by improved mixing methods.

7.5 Product quality, productivity and eradication of scale build up.

One of the prime drivers within Tecan is product quality. The stencils being produced require a smooth surface finish in order that the solder paste, forced through the apertures, releases well.

Without regeneration it was found that the surface finish deteriorated during manufacture to a point that the product was unusable. This usually occurred within 3 to 4 weeks. The etchant was then replaced. With the oxygen (air) regeneration it was possible to maintain surface finish within expectable limits for the duration of the test which lasted over 45 weeks.

Figure 7.2 shows the Ra readings from the start and end of each of the base line tests and compares this with a random selection of samples taken during the oxygen regeneration experiments. This shows how, by selection of a mid-point pH the surface roughness was controlled around 0.6 μm. This was felt to offer a good compromise between the rough and unusable surface which occurs with pH values approaching zero and the risk of resist breakdown leading to product defects at very low pH's.

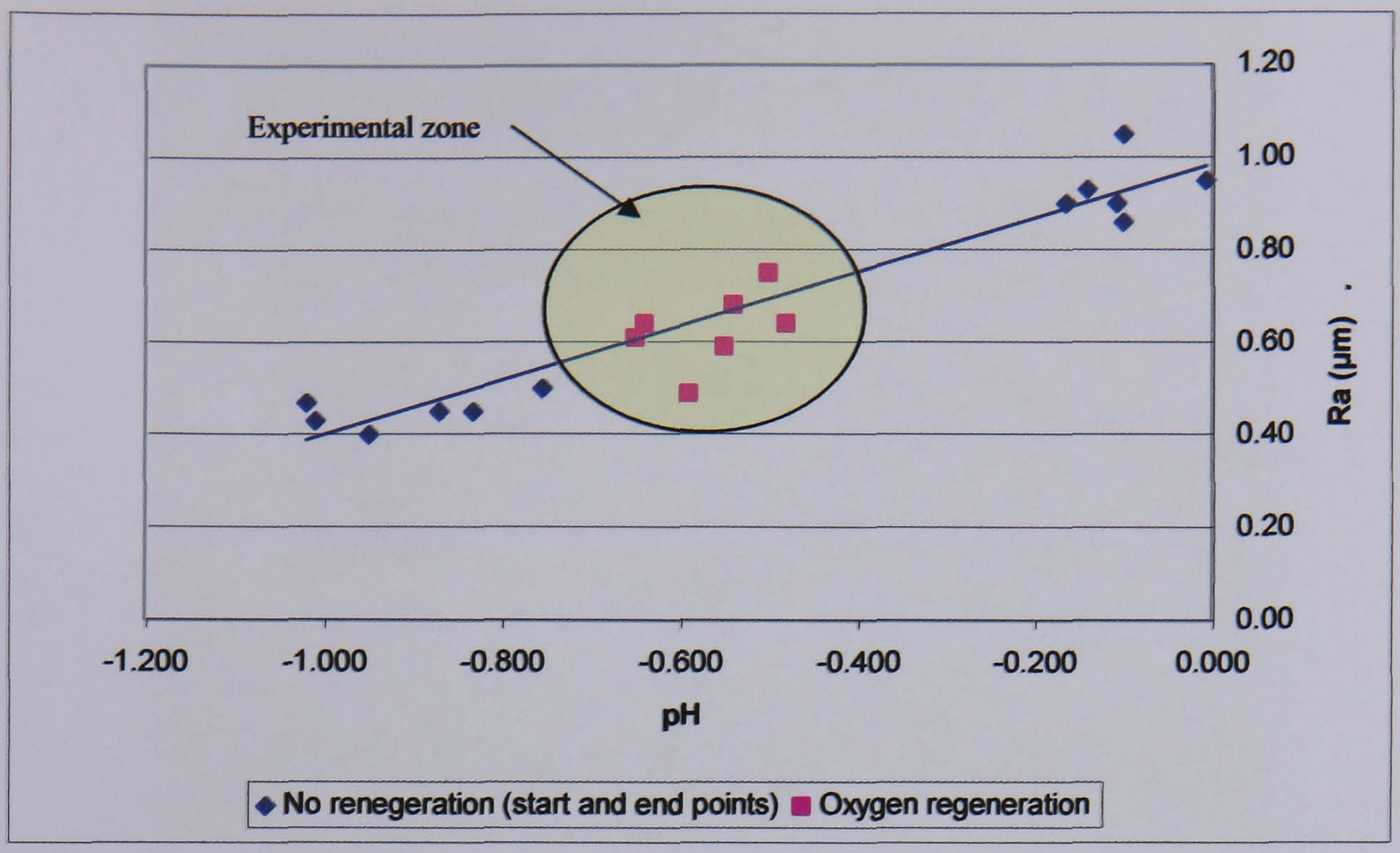


Figure 7.2 Surface roughness results from baseline and oxygen/air regeneration experiments

The photographs in Figures 7.3 and 7.4 show the poor definition and surface finish which were seen at the very end of one of the base line assessment tests. The surface finish was measured as 6 µm Ra. This is outside the normal range of operation of the etchant but is included to show how poor the surface finish can become without free acid control. The pH had by this point reached +0.1 indicating that very little if any free acid was present in the etchant. The product would not be usable, as the solder paste which the product is designed to print, would not release from such badly formed apertures. In comparison Figures 7.5 and 7.6 show a typical part produced during the oxygen regeneration study. It can be clearly seen that the definition of the apertures and surface finish are far better. The surface finish actually measured 0.49 µm Ra. The final two SEM's (Figures 7.7 and 7.8) show a part etched with etchant with a pH of -1.1 and whilst this obviously has a superior surface finish there is a very real risk of breakdown, as previously discussed. This would make the product as unusable as one with poor surface finish since the printing process for which these parts are used also relies on good edge definition.

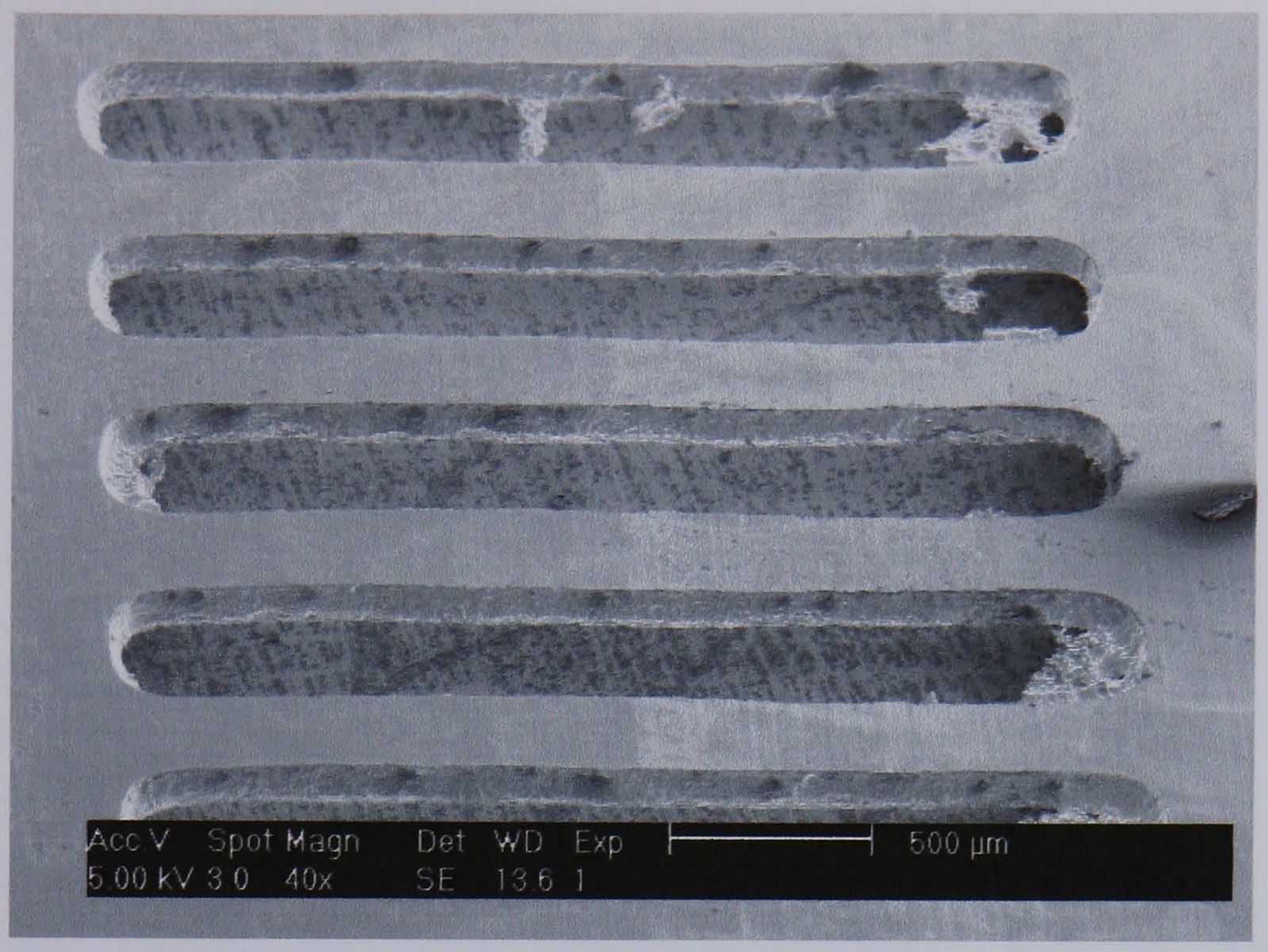


Figure 7.3 Poor aperture definitions seen at the end of a baseline etchant test

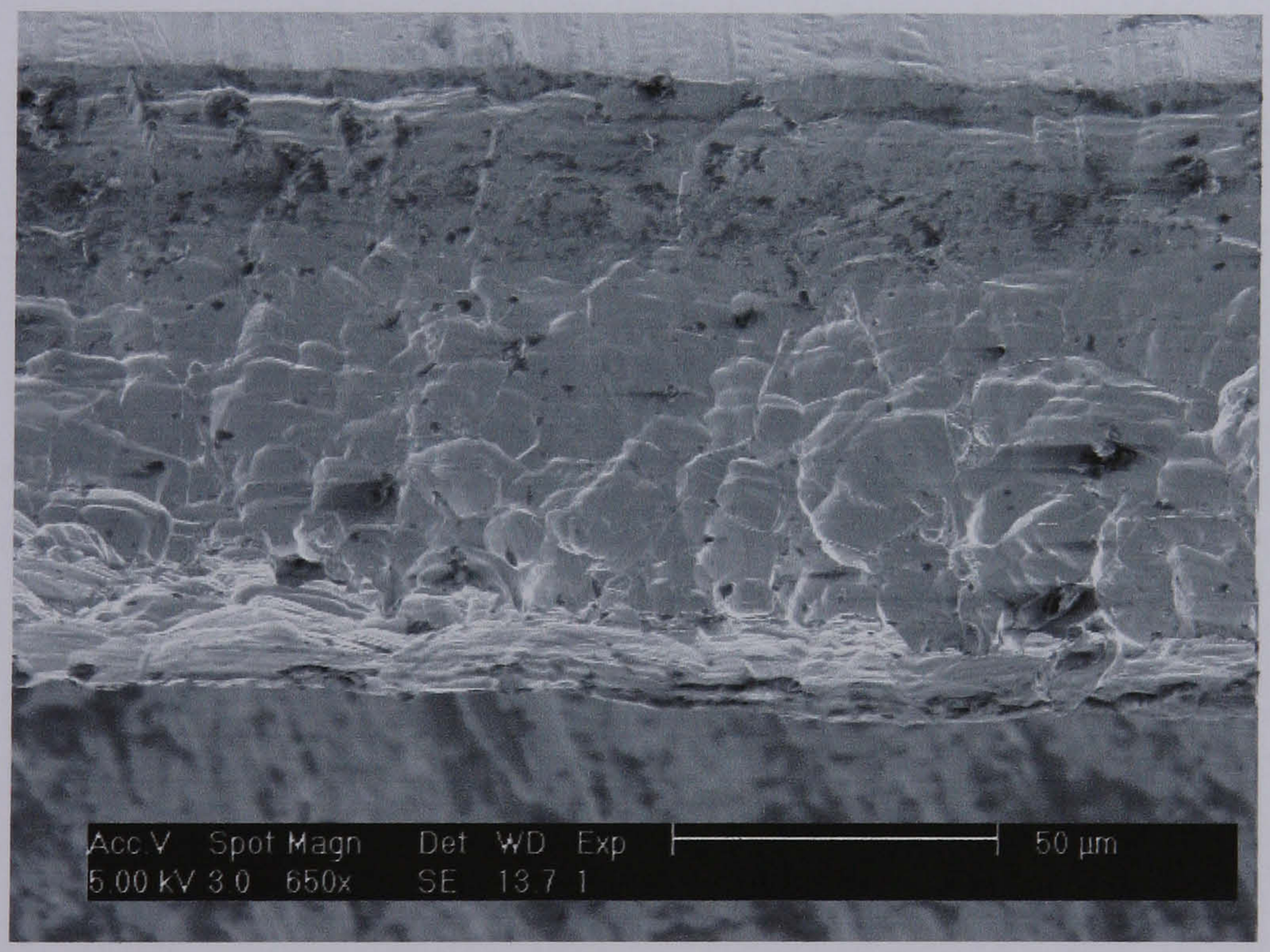


Figure 7.4 Poor side wall of an aperture seen at the end of a baseline etchant test

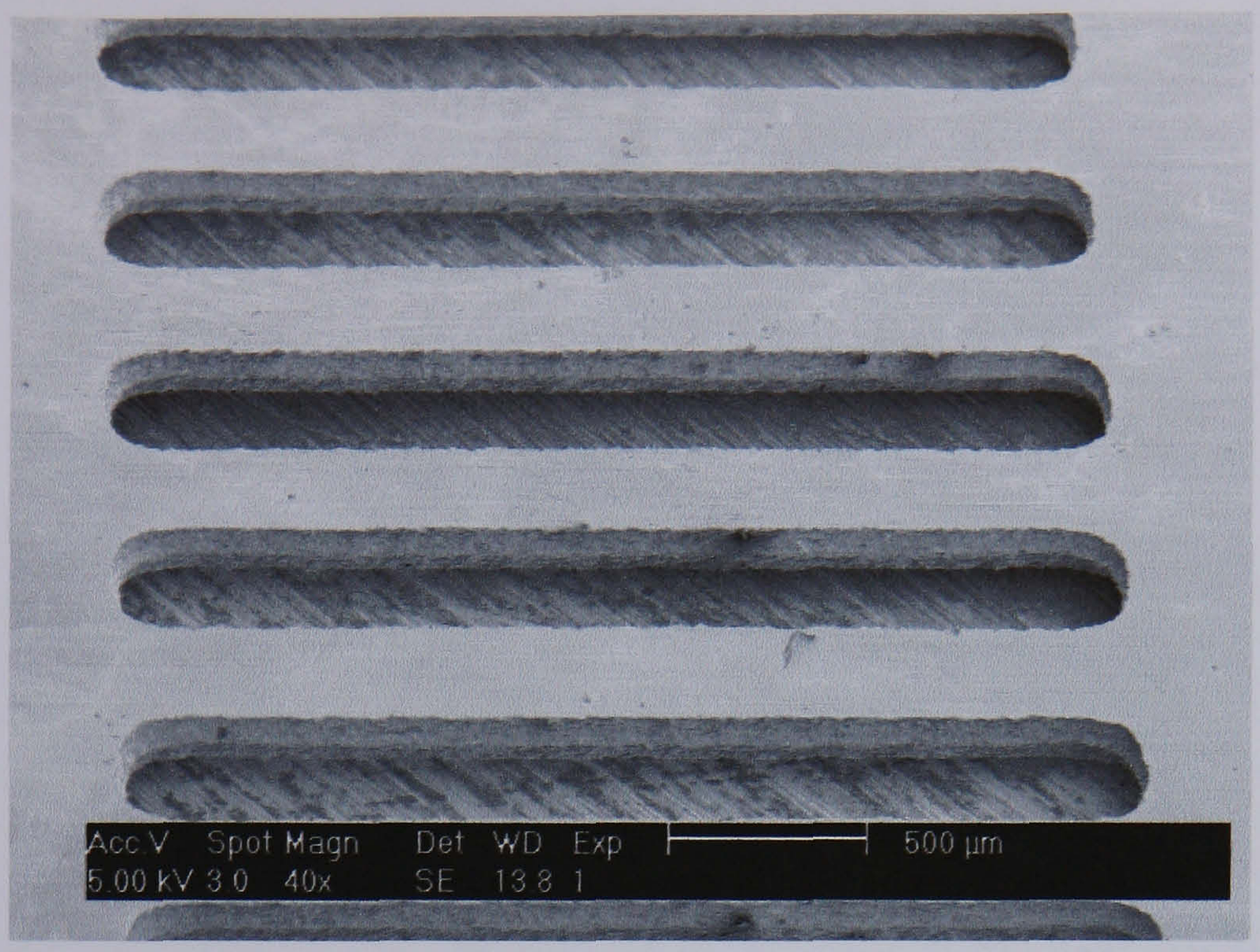


Figure 7.5 Typical aperture definitions seen during oxygen/air regeneration tests.

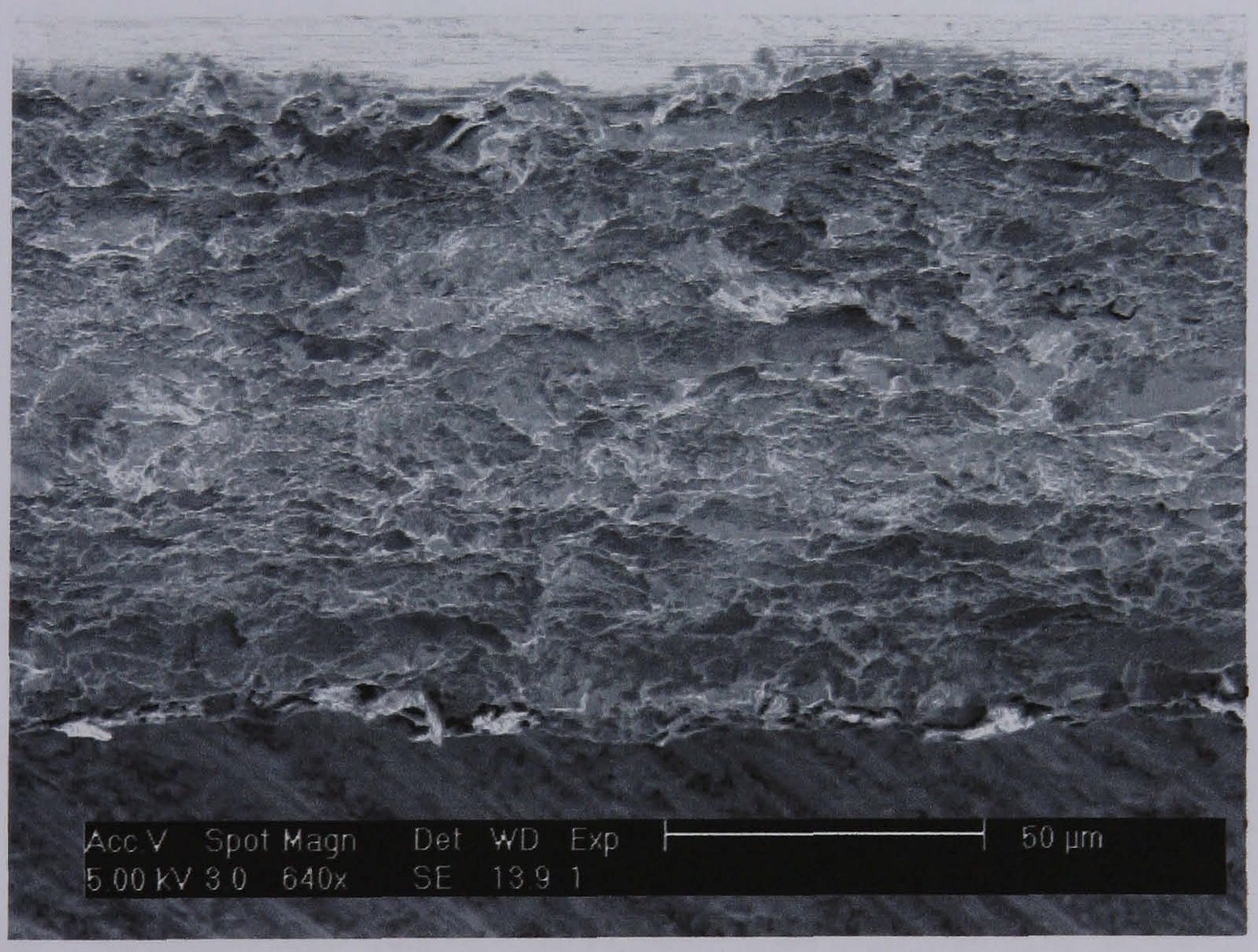


Figure 7.6 Typical side wall of an aperture seen during oxygen/air regeneration tests.

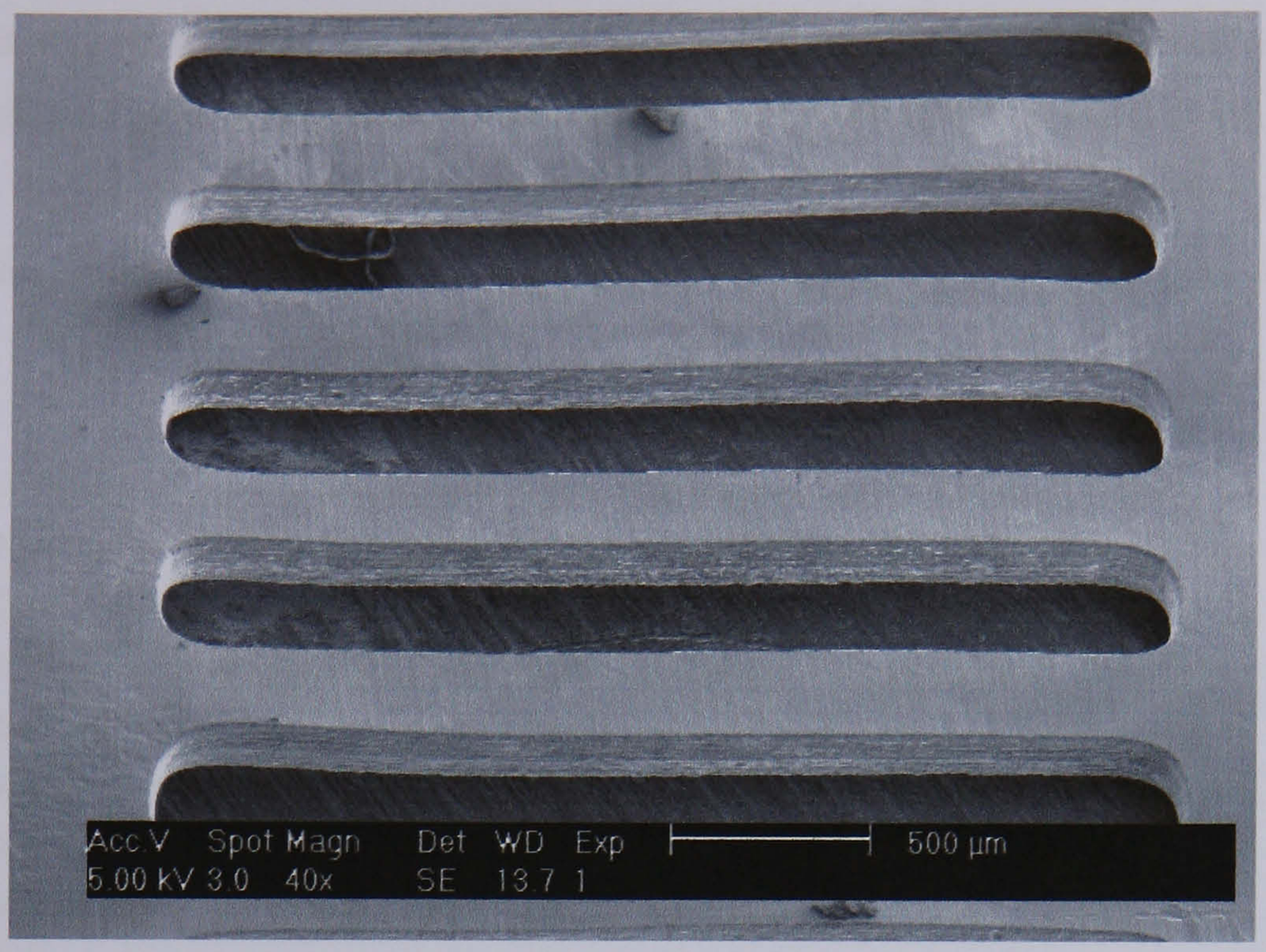


Figure 7.7 Typical aperture definitions of a part etched with high free acid levels

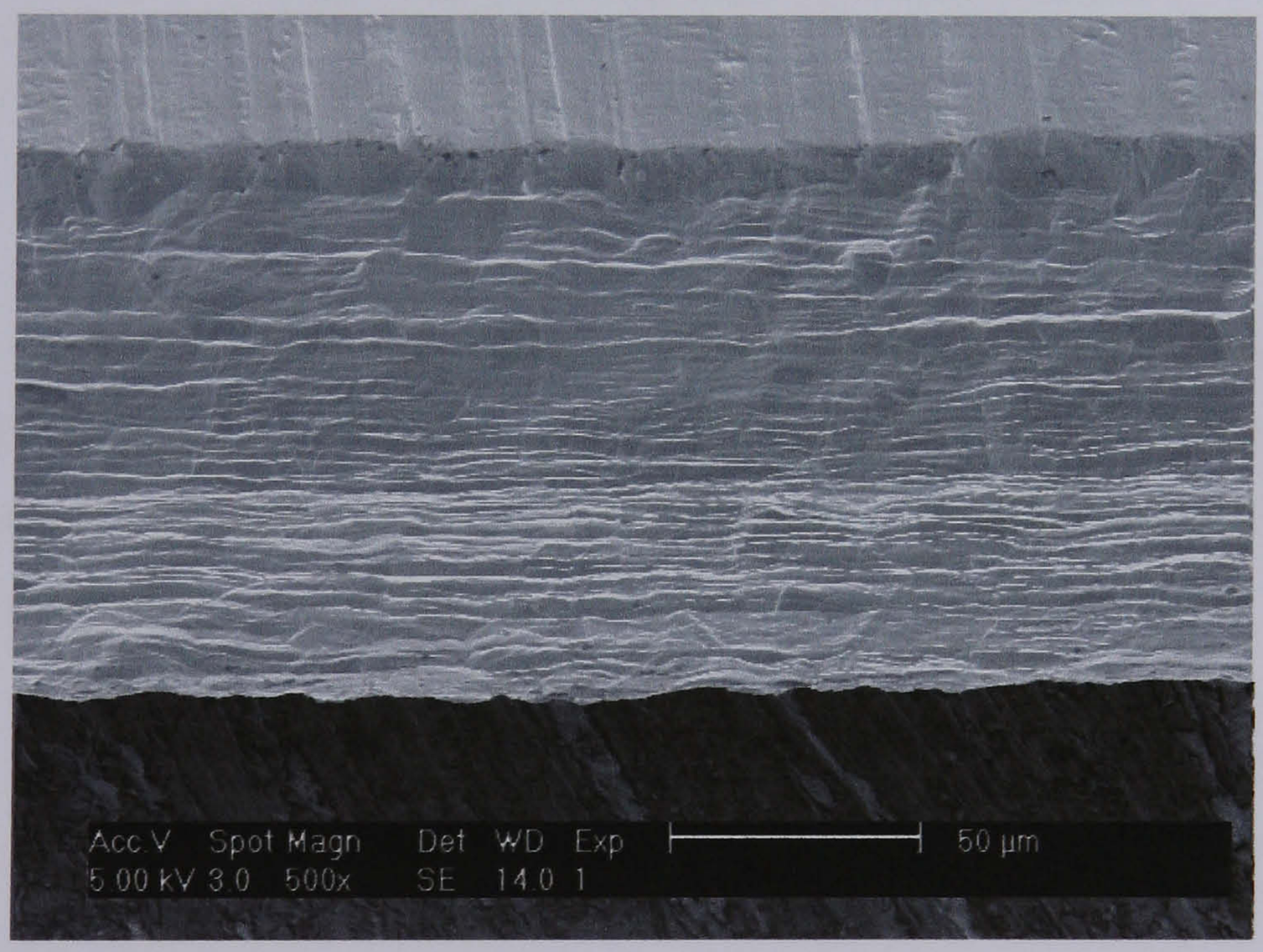


Figure 7.8 Typical side wall of a part etched with high free acid levels

Etch speed is another key factor which determines the product quality. Any variation in the etch speed will affect the rate at which metal is removed. If this is not taken into account when the machine speed is set, too much or too little metal will be removed and this in turn will affect the size of apertures being produced. Incorrect sizing of

apertures was one of the key reasons for rejects prior to the regeneration study. It will be seen from Figure 7.9 that the etch rate was controlled within tighter limits than was the case during the base line tests. The effect of this was that the operators were able to run the machine without continual manual intervention and with less chance of rejects.

Figure 7.9 Etch rate during extended oxygen/air regeneration tests clearly showing the consistency in etch rate that was achieved.

Similarly, the ORP of the solution was controlled within tight limits. This is shown in Figure 7.10. Whilst the actual value of the ORP is lower than that at the start of the etchants' use, the fact that it is stable results in far easier control of the etching process and better product.

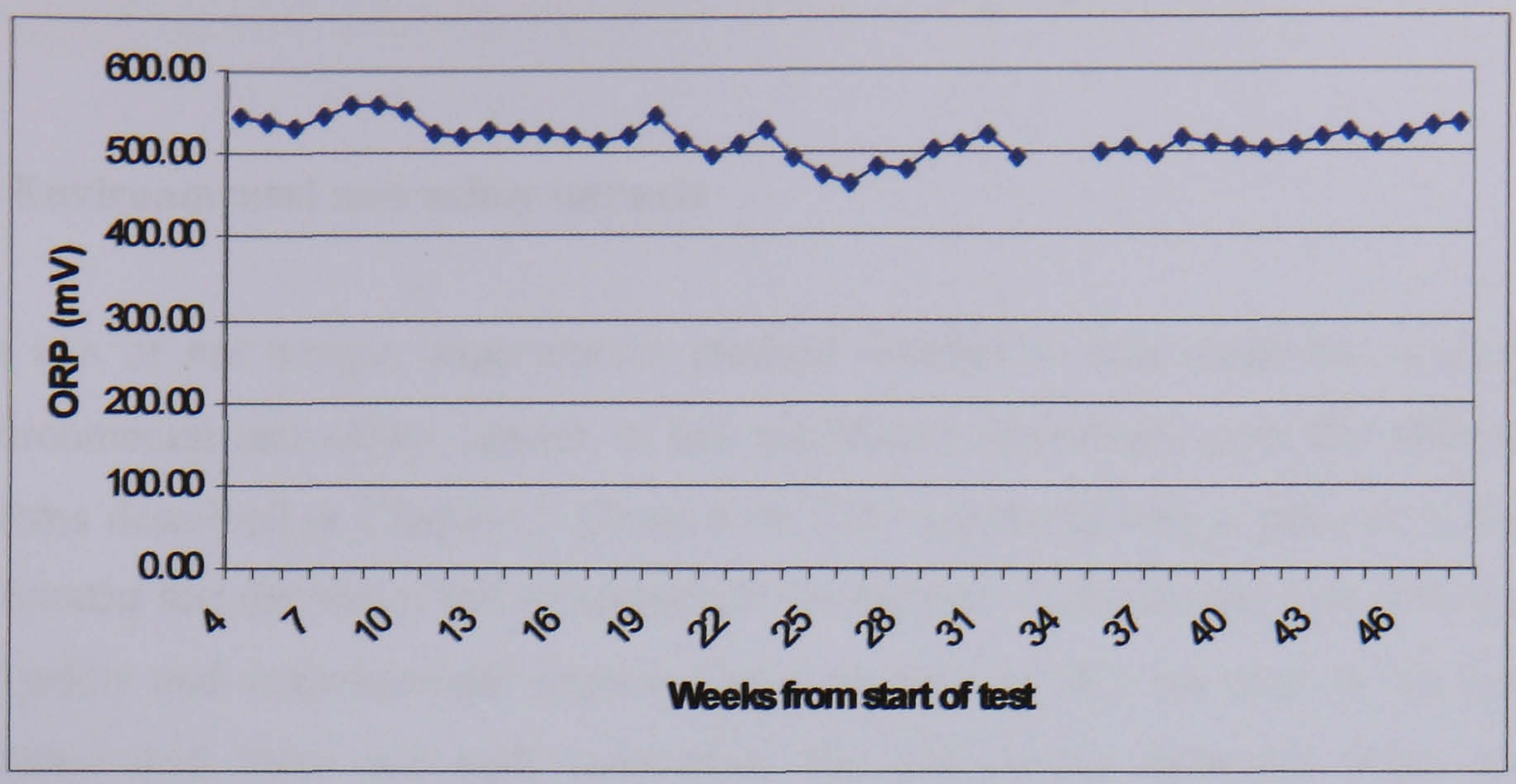


Figure 7.10 ORP during the oxygen/air regeneration test.

The build up of scale was a significant problem at Tecan when BEAC regeneration was used. This scale built up around all surfaces of the machine. It had the form of a very hard light grey deposit that was extremely difficult to remove and did not readily dissolve in any chemical suitable for use in the etching machine. If any of the scale broke off, it was transferred via the machine pumps to the spray bars where it blocked jets thus affecting product quality. Analysis of this scale showed it to be mainly oxides of silicon, however some reports of it being magnetic have also been made which would suggest it also contains iron [Andrews 2002 and Allen, Impey 2003]

This scale was not noticed during any of the oxygen/air regeneration work. This offers a number of significant advantages, including:-

- Reduction in the blocking of jets and hence improved product quality.
- Reduction in heating and cooling costs, since the scale insulates the elements of the machine which monitor and control temperature, i.e. heating elements, cooling coils and thermostat probes.
- Easier cleaning of the machine when etchant is changed.

7.6 Environmental and safety impacts

The use of the oxygen regeneration method detailed in this study has a positive environmental and safety impact. It has significant advantages over the alternative systems described in Chapter 2. Oxygen (at 21% concentration) is present in the air we breathe and the use of this to regenerate the etchant obviously has a positive health and safety and environmental impact. Small amounts of HCl are used in the system designed and these are well controlled, the acid being delivered from sealed containers by a simple pump system.

Other health, safety and environmental improvements are derived from the following areas:-

- Reduced chemical usage.
- Reduced waste disposal.
- Reduced product scrap.
- Reduced energy consumption due to:-
    - Elimination of the need to cool and heat ferric chloride when it is replaced, as would be the case without regeneration.
    - Reduced scale build up around heaters and cooling coils resulting in improved heating and cooling efficiency.
- Improved safety due to the reduction in both the amount and handling of hazardous chemicals

7.7 Summary of research findings

The table below summarises some of the key findings of this research.

	No regeneration	BEAC regeneration	Oxygen/air regeneration
Cost	High (£17.91)/Kg of metal etched	Medium (£7.82) /Kg of metal etched	Low (£2.97) /Kg of metal etched
Product tolerance	Variable dependent on etchant quality	Stable	Stable
Scale	No scale	Considerably build up of hard silica based substance.	No scale
Surface roughness	Variable dependent on etchant quality	Stable	Stable
Acid colour	Dark golden brown	-	Dark green/brown
Environmental impact	High	Medium	Low
Life of etchant	Short – typically 3 to 4 weeks	Long – typically 6 months to 1 year	Long – typically 6 months to 1 year
Volume of metal which can be etched	Only 15kg per 1000 litres of acid. i.e. one fill of the machine	In the region of 1000 kg per year	Tested to 500kg per year

	Before study	After study
Analysis of etchant	Largely considered a 'Black art'	Using ORP and pH it is possible to predict the behaviour of the etchant
Monitoring	Considered impractical in production situations. Too expensive and difficult to achieve.	Cost effective and simple to install and operate
Use of air	Not studied in any scientific depth.	Air can be used to regenerate etchants.

Table 7.1 Key findings from research

A paper based on this research has been accepted for publication in the Annals of the CIRP, Volume 55/1, under the title 'An Economic, Environment-friendly Oxygen-Hydrochloric Acid Regeneration System for Ferric Chloride Etchants used in Photochemical'. At the time of printing this thesis the paper was in the press so no page numbers are available.

7.8 Recommendations for future work

This work has indicated that the static mixer had very little, if any, impact on the regeneration process. However, it is believed that such devices could be beneficial to the process if additional research was conducted into their use and installation. It is suggested that the following improvements should be considered:-

- Variations in the density and configuration of the mixer elements in the static mixer body.
- Variations on configuration of the mixer in the regeneration circuit. This should include increasing the return pipe length. It is strongly advised that the mixer is used in the vertical mode to improve mixing efficiency. One possible solution could be to add an additional mixer some distance from the first with a length of straight pipe coupling them. The length of this pipe would be determined by observations of the phase separation of the two elements.
- Experiments with the ferric chloride at a higher temperature. This would have to be carried out 'off line' i.e. away from the etching machine since the machines used can only run at a maximum of 56°C. The aim would be to increase the rate of the reaction and hence improve the overall efficiency of the reaction.

By a combination of the above methods, it may be possible to regenerate the etchant used in higher metal removal rate situations; more than the 10kg per week possible during this study.

In addition to further research around the use of the static mixer, it is felt that additional research work could be conducted to advance the monitoring and control of the etching process. Some possible areas for further research are:-

- **Studies into the monitoring of metal loading.** Whilst this study was underway, research has been ongoing at Cranfield which has indicated

that microspectrometery has potential for monitoring the levels of metal dissolved into solution within the etchant. [Allen, Almond and Maynard 2004]. It would appear highly practical to add this type of measurement system to the sampling loop which would give the potential to monitor another critical parameter of the etchant.

- **Improvements in the sampling systems.** With a view to reducing the cost and possibly allowing more than one machine to be monitored, a sampling loop similar to the design given in Figure 7.11 could be considered. In this system a sampling loop would be fitted to each etching machine. A bleed point would be fitted into this loop which would feed etchant to the sampling chamber at regular intervals. This ensures that a representative sample is measured from each machine. It is not felt that conductivity should form any major part of the sampling system since the variations in conductivity brought about by metal loading complicate the true understanding of the measurement.

- **Research into the removal of the scale deposits**. These deposits are thought to be metallic in nature and a very simple test has shown that they are attracted to magnetic fields. It would therefore seem probable that some magnetic system could be developed for their removal.

- **Investigation into the removal of other metal contamination** such as Cr and Ni which are not regenerated, possibly by filtration.

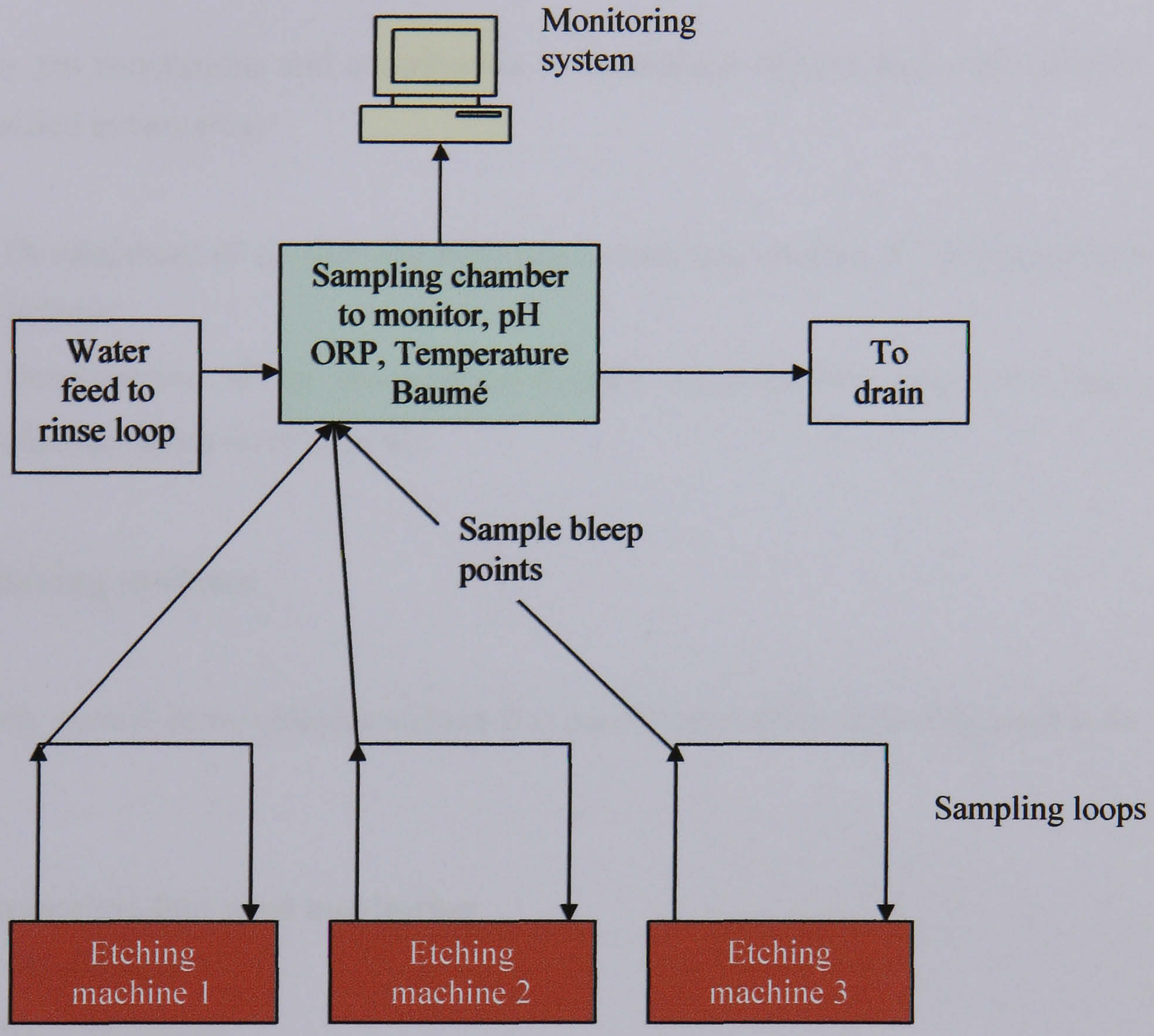


Figure 7.11 Schematic diagram of proposed sampling system

8.0 Conclusion

8.1 Introduction

In summary the conclusions and contribution to knowledge derived from this research can be classified in two areas:

- Development of on-line and real-time monitoring systems for ferric chloride etchant.
- Development of an environment-friendly regeneration system for ferric chloride based on oxygen/air.

8.2 Monitoring systems

To effectively control ferric chloride etchant it is concluded that the following need to be monitored

Critical parameters that need monitoring

- Temperature
- Specific gravity
- ORP
- Free acid (best monitored using pH)

This monitoring would preferably be achieved using real time analysis that also allows date to be captured for future examination. All of these parameters will need monitoring since they interact considerably with each other. Therefore, this interaction needs to be considered when the data is analysed.

Benefits of monitoring using real-time and on-line methods:

- Elimination of the need for manual titration, which is prone to human error and is very time consuming.
- Allows accurate additions of chemicals, minimising process variations.
- Easy identification of etching equipment faults.
- Improved productivity.
- Reduced defects due to acid related faults.

8.3 Regeneration of etchant with Oxygen / Air

An Oxygen-based regeneration has been successfully developed and used for 18 months. The process has resulted in numerous economic and quality improvements, which can be summarised as:

- A saving of £7000 per year per machine.
- Product defects due to variation in etchant condition have been reduced by 15%
- Lower environmental impact due to reduced chemical usage and disposal.
- Elimination of scale build up which affects both product quality and cost.
- Improved equipment reliability due to simplicity of the equipment used.

8.4 Published work

A paper based on this research has been accepted for publication in the Annals of the CIRP, Volume 55/1, 2006, under the title 'An Economic, Environment-friendly Oxygen-Hydrochloric Acid Regeneration System for Ferric Chloride Etchants used in Photochemical Machining'. At the time of printing this thesis the paper was in the press so no page numbers are available.

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GCE – O Level Passbook in Chemistry, C W Capham, Intercontinental Book Productions, Seymore Press Ltd London ISBN 085047 905 3

GCE – A Level Passbook in Chemistry, J E Chandler and R J Wilkinson Intercontinental Book Productions, Seymore Press Ltd London ISBN 085047 921 5

Working instructions for ABB pH and metal electrodes, application notes from ABB Instrumentation Ltd, Gloucester England,

Glossary of terms

Baumé	Measure of specific gravity – the density of a substance relative to some other reference usually water. There are two scales used, heavy and light Baumé. Heavy is used for liquids heavier than water, such as ferric chloride. The Term Baumé relates to the French chemist who developed the system Antoine Baumé.
Acid	A substance which, when dissolved in water, forms a solution with a pH less than. The etchant used to dissolve the substrate, in this study the etchant is Ferric Chloride
AA	Atomic Absorption spectrometry used to analysis solution to determine the metal content.
Anode	The positive electrode in an electrolytic cell.
CAD	Computer Aided Design (or Drawing) utilised to produce engineering drawings associated phototooling files for photoplotters.
Chlorine Regeneration	Used to regenerate ferric chloride to maintain good quality acid for the etching process.
Chrome on Glass	Phototool used for precise and accurate work.

Coat	To cover or apply to a substrate surface a layer of a photoresist material by dipping rolling, spraying, laminating, spinning, printing, or flowing.
Develop	To subject photosensitive material to a chemical treatment designed to produce a usable image in matter previously modified by radiation
Dip Coating	Applying resist to the surface of the substrate by immersing it in a tank of liquid resist and slowly withdrawing.
Dry Film Resist	Photoresist supplied in a sheet laminate form as rolls
Electroforming	The growing of metal in an electroplating bath on a mandrel (solid/wax/polystyrene, etc.) according to Faraday's Laws of Electrolysis.
Etch Allowance	The total dimensional adjustment, expressed in inches, mils or millimetres per side incorporated into the design of an artwork/phototool for photochemically machined part to compensate for the etching process.
Etch Factor	The ratio of the etched depth to the lateral etch, or undercut.
Etchant	Chemical solution used in etching
Exposure (E)	The quantity of light received per unit area of the layer. Exposure may be specified in terms of intensity, spectral composition and duration.

Ferric Chloride	The most common etchant used in PCM.
Laser Plotter	A precision optical-mechanical system for producing phototools on film or glass. Alaser beam scans the surface and is turned on or off to expose (or not expose) the photographic emulsion. A PC and special software control this scanning operation.
Liquid Resist	A photoresist applied to the substrate by dipping, roller coating, curtain coating or spraying. Liquid resists are most often photopolymers. In rare high volume applications casein is used
Mil	One-thousandth part of one inch (U.S. term)
Negative-working Resist	A resist which is polymerized (hardened) by light and which after exposure and development remains on the surface of the substrate in those areas which were beneath the transparent parts of photomask
ORP	Oxidation Reduction Potential. Often used as a measurement to assess the power of an etchant
PCM	Photo Chemical Machining
PEF	Photo Electro Forming
pH	A number used to express degrees of acidity or alkalinity in solution.

Photo Chemical Machining	PCM. The process of using photoresist to preserve the surface of metal, while using an etchant to dissolve away bare metal from both sides, thereby manufacturing components.
Photo Chemical Machining Institute	PCMI. The trade association for the Photo Chemical Machining industry.
Photopolymer	Polymeric material sensitive to actinic radiation.
Photoplotting	The photographic process whereby an image is generated by the motior and/or postioning of a controlled light beam by numerical control directly onto a light sensitive material (usually emulsion).
Photoresist	A material which, when properly applied to any of a variety of substrates, becomes sensitive to portions of the electromagnetic spectrum and, when properly esposed and developed, masks portions of the substrate with a high degree of integrity
Phototool	The working tool that is used in production for exposing the resist coated work piece.
Positive-working Resist	A resist which is decomposed by light and which, after esposure and development, is removed from those areas which were beneath the transparent parts of a production master.
Redox	The reduction-oxidation potential in an electrochemical reaction involving the transfer of electrons between different chemical species.

SEM	Scanning Electron Microscope.
Smut	Fine, dark-coloured, powdery material that sometimes remains on the surface of pickled or etched metal inadequately rinsed
Spin Coating	A method of putting a precise thickness of a wet resist coating on a substrate.
Thou	An English abbreviation for one-thousandth of an inch.
Undercutting	Lateral etching into a substrate under a resist coating.
Ultraviolet	Invisible electromagnetic radiation defined between 100 and 380mm.
Yellow Room	An area illuminated with yellow light for handling photo resist coated panels with minimal potential for exposing the coating. The yellow illumination is provided by special fluorescent tubes, coloured sleeves which slop over conventional fluorescent tubes, or yellow plastic filter materials that cover fluorescent lighting fixtures.
Chlorine gas	A poisonous greenish yellow gas (Cl_2). Chlorine occurs widely in nature as sodium chloride (as seawater). It is manufactured by the electrolysis of brine and is a strong oxidising agent. Applications include the chlorination of drinking water, bleaching and in the manufacture if organic chemicals.
Electrolysis	The production of a chemical reaction by the passage of current through an electrolyte. Positive ions migrate to the cathode and undergo reduction and negative ions to the anode and undergo oxidation.

Free acid content	In $FeCl_3$, some 'Free' acid (HCl) content arises through the reaction between H^+ ions in the aqueous phase and chloride ions from the $FeCl_3$. However, more is usually added to provide an extra source of chloride ions during etching and thus prevent dissolved metal species from precipitating out as metal hydroxides
Hydrolysis	A chemical reaction caused by dissolution of a compound in water.
Ions	An atom or group of atoms that has either lost one or more electrons, making it positively charged (a cation) or gained one or more electrons making it negatively charged (an anion).
Molarity	Measure of gram-molecular weights of a compound present (dissolved) in 1 litre of solution.
Molecular weight	Molar mass of a species in grams per mole.
Oxidation	A chemical reaction involving the loss of electrons.
Ozonolysis	In the context of etchant regeneration, this is an oxidation reaction performed by the bubbling of ozone, through the spent etchant.
Photochemical Machining (PCM)	A multi-stage manufacturing technique involving selective removal of metal by chemical etching.

Photoresist	A photo sensitive coating placed on the metal substrate during the PCM process. Exposure to UV light will cause chemical changes to exposed areas of resist, thus making it either vulnerable to developing solution or inert to it. (This depends on whether the resist is positive or negative working). The developed resist will protect the substrate against etching.
Phototool	Used in the PCM process. A highly resolution image placed over the photoresist coated substrate, prior to exposure by UV light. The phototool protects selected areas of the resist from subsequent chemical changes as the result of UV.
pH scale	A logarithmic scale for expressing the acidity or alkalinity of a solution .
Precipitation	The formation of a suspension of small solid particles in a liquid by chemical reaction.
Redox Potential (ORP)	The relationship between the activities of the oxidised and reduced species in a chemical reaction. As an approximation, the respective concentrations of the ionic species can be substituted for their activities. ORP is measured in V (volt) or mV (millivolt).
Reduction	A chemical reaction involving the gain of electrons.
Regeneration	A process in which a reduced ionic species is converted back to the oxidised form. For example, in used $FeCl_3$, ions from the original total $FeCl_3$ that have been reduced to Fe^{2+} ions are oxidised to Fe^{3+}.
Standard Electrode Potential (E^0)	The potential for a given cell measured when the current flow is essentially zero and all ions and molecules in the solutions are at a concentration of 1M and all gases at a pressure of 1 atmosphere.

Stoichiometry This describes chemical reactions in which the reactants combine in a simple whole number ratios. A stoichiometric mixture is one that give rise to no excess reactant.

Spent Etchant Etchant in which the active ionic species has been reduced to such an extent that the rate of etching and surface characteristics of the etched substrates become unacceptable.

Appendix 1

Materials and etchants

The following tables give background information about the etchabiliy of commonly used materials, together with an indication of typical etchants used in industry to produce parts

Etchability			
Good	**Good to Fair**	**Fair to poor**	**Poor**
Copper	Austenitic s/s	Molybdenum	Tunsten
Copper Alloys	Ppt. hardening s/s	Nichrome (Ni, Cr)	Hastelloy C
Zinc	Martensitic s/s	Vanadium	Titanium
Carbon steel	Ferritic s/s	Chromium	Niobium
Kovar (Fe, Ni Co)	Inconel (Ni, Cr, Fe)	Lead	Tantalum
Nickel		Manganese	
Nickel alloys		Rhenium	
Magnesium		Zirconium	
Aluminium			

Table A1.1 Comparison of commonly used engineering materials and their relative suitability for etching in standard spray etching equipment. [Allen 1986]

Material	Typical etchant
Silver	Ferric nitrate Nitric acid
Gold	Potassium iodide and iodine Aqua Regia (conc. HCl and conc. HN03 – 3:1 by vol)
Platinum	Aqua Regia
Titanium	HF-based etchant
Molybdenum	Potassium ferricynide Ferric nitrate
Chromium	Potassium ferricynide

Table A1.2 Some typical etching solutions used to etch more corrosion resistant materials. [Allen 1986]

Appendix 2

Selection of Phototooling

The table below shows some of the key factors which influence the selection of photo-tool for use in the PCM process.

Film work type	Substrate material	Image material	Thermal coefficient of substrate	Humidity coefficient of linear expansion (%/%RH)	Relative cost
Film or soft tool	Cellulose triacetate	Silver halide emulsion	0.0055	0.005 – 0.010	Low
Film or soft tool	Polyethylene terephthalate (polyester)	Silver halide emulsion	0.0019	0.002 – 0.004	Low
Glass or hard tool	Float glass	Chrome	0.0010	0	High

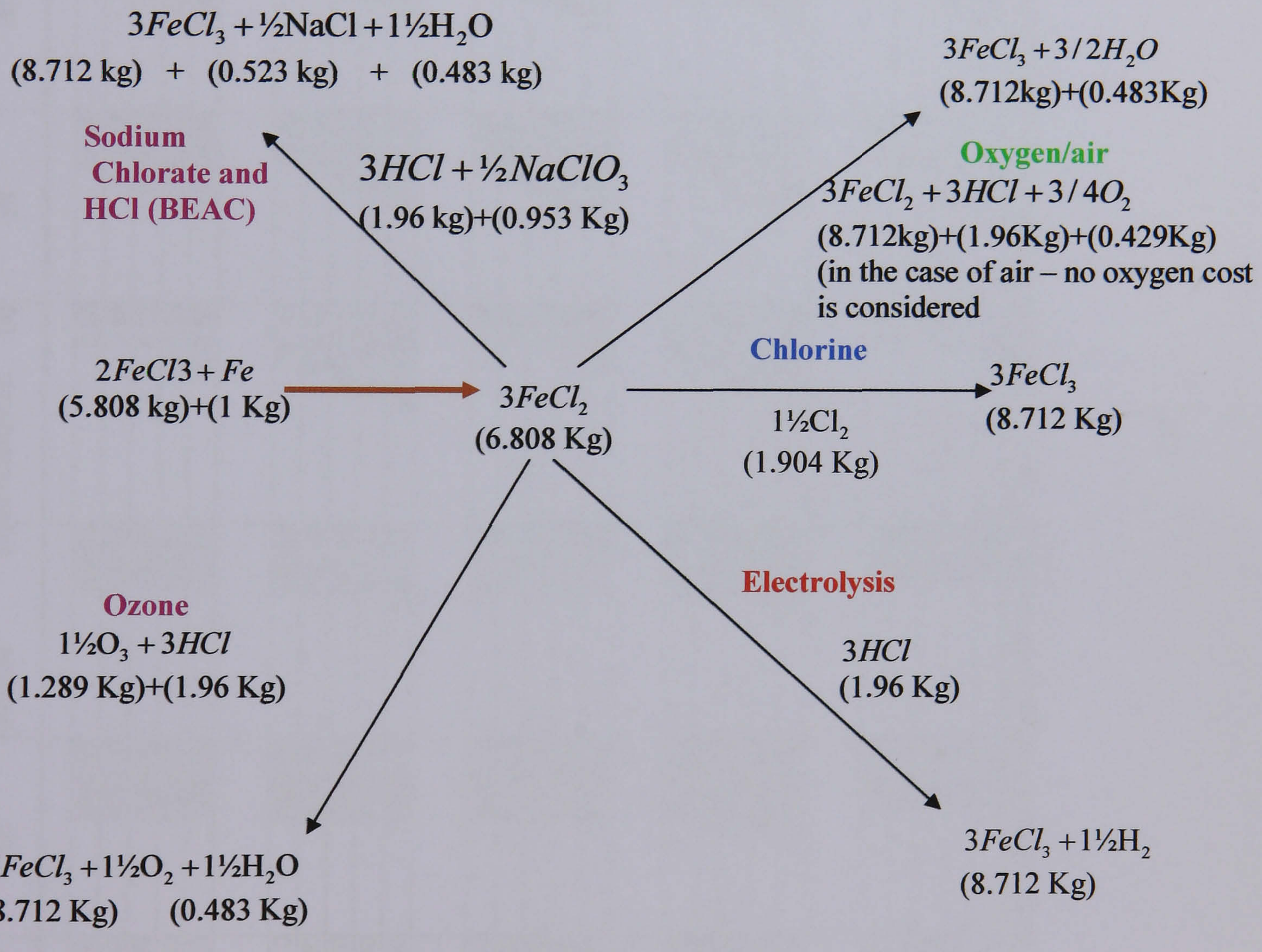
Table A2.1 Comparison of various photo-tools [Berket-Wendis 2003 and Agfa]

It should be noted that the cellulose triacetate film is the oldest method and in fact is seldom used. The more modern polyethylene terephthalate films also offer considerable advantages in terms of line quality and resolution. The very latest generation of these films are offering image qualities which compare very favourably with chrome on glass tools. However the issue of lower stability of film tools will always be a limiting factor. In terms of image durability the chrome on glass is tougher and less likely to be scratched in use. However the glass substrate is obviously prone to breakage.

Appendix 3

Theoretical regeneration cost calculations

The chart shown in chapter 2 (Figure 2.16) was derived from the stiochiometric equation given below, the table on the following page details the calculations for each method. In calculating the costs for the oxygen system, the oxygen used is that available form ambient air so has zero cost since it is assumed that the spray method is used, therefore no compression or delivery costs are required.



Method	Weight of iron etched in one year (kg)	Equipment cost [1]	Maintenance charges [2]	Power consumption [3]	Chemical cost [4]	Disposal cost [5]	Total cost (£)	Cost of regeneration (£/kg)
						[8]		
BEAC	10	1000.00	100.00	0.04	51.06	32.64	1183.74	118.37
[6]	100	1000.00	100.00	0.43	510.56	326.39	1937.37	19.37
	1000	1000.00	100.00	4.33	5105.56	3263.85	9473.74	9.47
	10000	1200.00	120.00	43.26	51055.60	32638.50	85057.36	8.51
	100000	1200.00	120.00	432.60	510556.00	326385.00	838693.60	8.39
						[9]		
Electrolysis	10	7600.00	760.00	85.44	10.52	19.89	8475.85	847.59
[7]	100	7600.00	760.00	854.40	105.24	198.90	9518.54	95.19
	1000	7600.00	760.00	8544.00	1052.41	1989.00	19945.41	19.95
	10000	9740.00	974.00	85440.00	10524.14	19890.00	126568.14	12.66
	100000	12800.00	1280.00	854400.00	105241.38	198900.00	1172621.38	11.73
						[10]		
Chlorine	10	5122.00	512.20	0.06	33.89	25.67	5693.82	569.38
	100	5122.00	512.20	0.62	338.87	256.73	6230.42	62.30
	1000	5122.00	512.20	6.23	3049.83	2567.25	11257.51	11.26
	10000	5122.00	512.20	62.28	27448.47	25672.50	58817.45	5.88
	100000	5122.00	512.20	622.75	222332.61	256725.00	485314.56	4.85
						[11]		
Ozonolysis	10	3200.00	320.00	45.10	10.51	21.96	3597.57	359.76
[7]	100	4480.00	448.00	451.00	105.08	219.60	5703.68	57.04
	1000	5120.00	512.00	4510.00	1050.76	2196.00	13388.76	13.39
	10000	41600.00	4160.00	7849.00	10507.60	21960.00	86076.60	8.61
	100000	134000.00	13400.00	78490.00	105076.00	219600.00	550566.00	5.51
						[12]		
Oxygen/air	10	900.00	90.00	0.04	12.60	32.64	1035.28	103.53
	100	900.00	90.00	0.43	126.00	326.39	1442.82	14.43
	1000	900.00	90.00	4.33	1260.00	3263.85	5518.18	5.52
[13]	*10000*	*900.00*	*90.00*	*43.26*	*12600.00*	*32638.50*	*46271.76*	*4.63*
[13]	*100000*	*900.00*	*90.00*	*432.60*	*126000.00*	*326385.00*	*453807.60*	*4.54*

Table A3.1 Calculations for regeneration cost by various methods and for various quantities of etched metal.

The following assumptions and cost have been used in generating the table

[1] Based on 5 year deprecation
[2] Maintenance based on 10% of capital cost
[3] Power based on a rate of 7.12p/KWh
[4] Chemical costs based on HCL@ £0.218 /ltr Oxygen @£10/10m2 cylinder
Sodium chlorate @ £1.86 /ltr chlorine @ £1.87 /Kg
[5] Disposal cost based on a rate of £0.45/ltr
[6] Equipment cost £5000 for small model £6000 for large model
[7] Equipment cost taken from previous research (Allen 1991)
[8] Process will generate 7.253 l/kg of metal etched (Allen 1991)
[9] Process will generate 4.42 l/kg of metal etched (Allen 1991)
[10] Process will generate 5.705 l/kg of metal etched, for 40 Baume solution (Allen and Almond 1992)
[11] Process will generate 4.88 l/kg of metal etched, for 40 Baume solution (Allen 1991)
[12] Assuming waste generated wil be 7.253 l/kg of metal etched
[13] At these metal loading rates the system, could probably not regenerate at the required rate

N.B.

1. *At very high etch rates (above 1000kg/year) figures will be extremely dependant of the cost of chemicals and disposal changes which can very greatly at high volumes between different suppliers.*
2. *Figures shown are theoretical and will be effected by operating conditions*

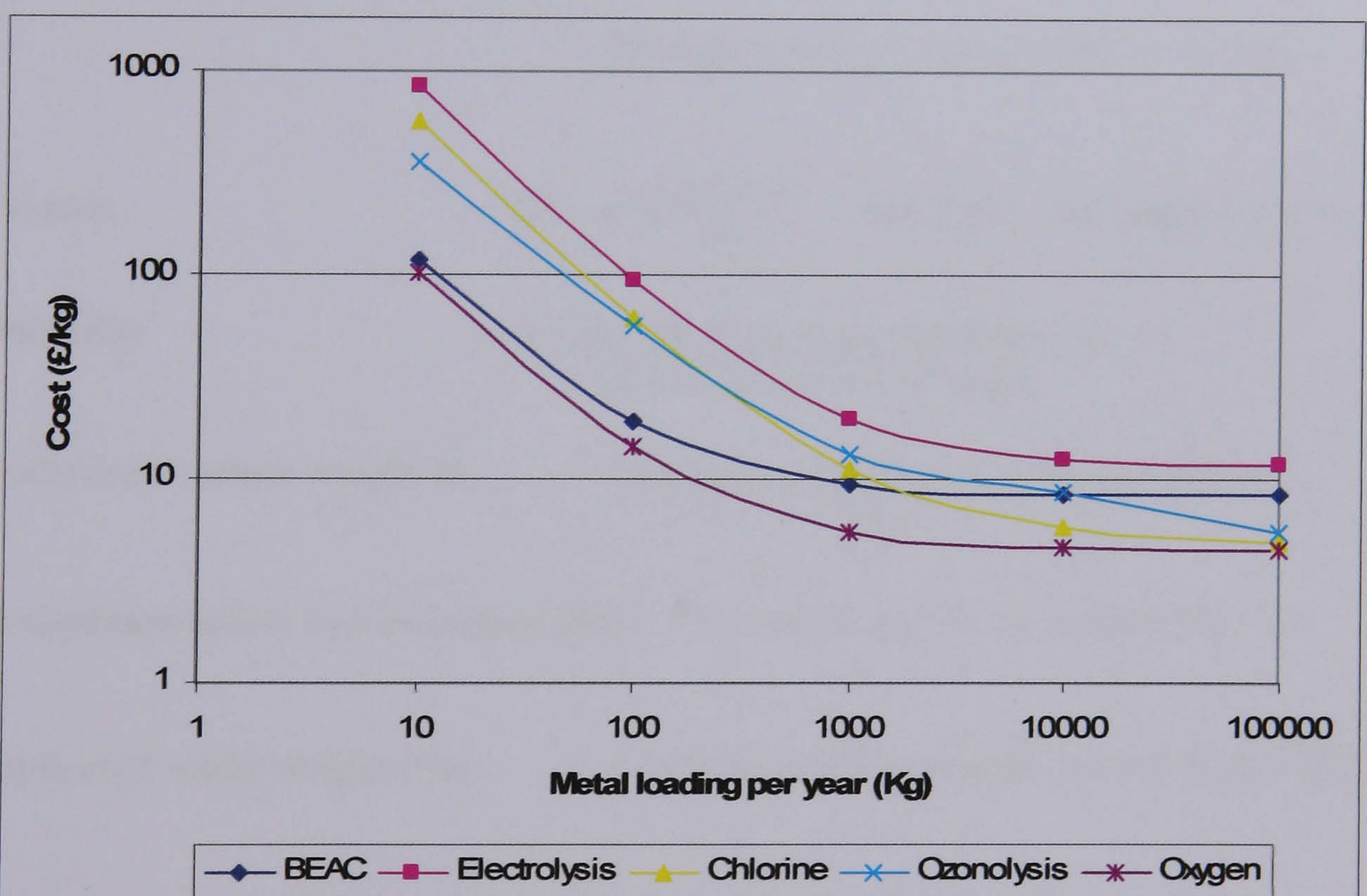


Figure A3.1 Cost comparison including oxygen regeneration

Appendix 4

Concentration of $FeCl_3$ solutions expressed in various formats

The following are the basic formulas used in the calculation of various parameters associated with the specification and, measurement of ferric chloride etching solution.

Key Figures

Molecular weight of $FeCl_3$ = 162.22

Molecular weight of hydrated $FeCl_3$ = $FeCl_3.6H_2O$ = 270.32

Basic formulas

Specific gravity $SG = \frac{\rho}{0.99823}$ where ρ = relative density at 20°C

(relative density of water at 20°C = 0.99823)

Baumé °Bé = $145\frac{(SG-1)}{SG}$ where SG = the Specific Gravity

Molarity = $\frac{\text{Anhydrous solute concentration (g/l)}}{\text{Molecular weight of solute}}$

Anhydrous solute weight % = $\frac{\text{Molarity x Molecular Weight of Solute}}{10\,\rho}$

Anhydrous solute concentration (g/l) = 10 x Anhydrous solute weight (%) x ρ

Hydrated solute weight (%) = Anhydrous solute weight (%) x 270.32/162.22

The following table gives a cross conversion for the various parameters using the formula given above. **[Allen, Almond and Bridges 2005]**

Specific Gravity @20°C	Density @20°C (g/cm^3)	Baumé (°Bé)	Molarity (mol/l)	Ferric concentration (Fe^{3+}) (g/l)	Anhydrous solute weight (%)	Hydrated solute weight (%)	Anhydrous solute concentration (g/l)
1.0043	1.0025	0.6	0.031	1.73	0.50	0.83	5.01
1.0086	1.0068	1.2	0.062	3.47	1.00	1.67	10.07
1.0171	1.0153	2.4	0.125	6.99	2.00	3.33	20.31
1.0256	1.0238	3.6	0.189	10.57	3.00	5.00	30.71
1.0341	1.0323	4.8	0.255	14.22	4.00	6.67	41.29
1.0426	1.0408	5.9	0.321	17.91	5.00	8.33	52.04
1.0500	1.0481	6.9	0.377	21.05	5.83	5.835	61.16
1.0512	1.0493	7.1	0.388	21.68	6.00	10.00	62.96
1.0600	1.0581	8.2	0.438	24.46	6.71	11.19	71.05
1.0687	1.0668	9.3	0.526	29.38	8.00	13.33	85.34
1.0700	1.0681	9.5	0.538	30.05	8.17	13.62	87.27
1.0779	1.0760	10.5	0.597	33.34	9.00	15.00	96.84
1.0800	1.0781	10.7	0.620	34.63	9.33	15.55	100.58
1.0872	1.0853	11.6	0.669	37.36	10.00	16.66	108.53
1.0900	1.0881	12.0	0.699	39.04	10.42	17.37	113.39
1.1000	1.0981	13.2	0.776	43.34	11.46	19.10	125.88
1.1059	1.1039	13.9	0.817	45.61	12.00	20.00	132.47
1.1100	1.1080	14.4	0.854	47.69	12.50	20.83	138.54
1.1200	1.1180	15.5	0.933	52.11	13.54	22.56	151.35
1.1248	1.1228	16.1	0.969	54.12	14.00	23.33	157.19
1.1300	1.1280	16.7	1.014	56.63	14.58	24.30	164.49
1.1400	1.1380	17.8	1.096	61.21	15.62	26.03	177.79
1.1440	1.1420	18.3	1.126	62.90	16.00	26.66	182.72
1.1500	1.1480	18.9	1.179	65.84	16.66	27.76	191.26
1.1600	1.1579	20.0	1.244	69.47	17.43	29.04	201.80
1.1636	1.1615	20.4	1.289	71.98	18.00	29.99	209.08
1.1700	1.1679	21.1	1.342	74.95	18.64	31.06	217.70
1.1800	1.1779	22.1	1.423	79.47	19.60	32.66	230.84
1.1837	1.1816	22.5	1.457	81.36	20.00	33.33	236.32
1.1900	1.1879	23.2	1.505	84.05	20.55	34.25	244.14
1.2000	1.1979	24.2	1.588	88.69	21.51	35.84	257.61
1.2100	1.2079	25.2	1.673	93.43	22.47	37.44	271.39
1.2200	1.2178	26.10	1.758	98.18	23.42	39.02	285.18
1.2256	1.2234	26.7	1.810	101.08	24.00	39.99	293.62
1.2300	1.2278	27.1	1.845	103.04	24.38	40.62	299.30

Specific Gravity @20°C	Density @20°C (g/cm^3)	Baumé (°Bé)	Molarity (mol/l)	Ferric concentration (Fe^{3+}) (g/l)	Anhydrous solute weight (%)	Hydrated solute weight (%)	Anhydrous solute concentration (g/l)
1.2400	1.2378	28.1	1.931	107.84	25.31	42.17	313.25
1.2500	1.2478	29.0	2.015	112.53	26.20	43.65	326.87
1.2600	1.2578	29.9	2.100	117.28	27.08	45.13	340.66
1.2700	1.2678	30.8	2.186	122.08	27.97	46.61	354.61
1.2800	1.2777	31.7	2.271	126.83	28.83	48.05	368.40
1.2900	1.2877	32.6	2.355	131.52	29.67	49.44	382.03
1.3000	1.2977	33.5	2.440	136.27	30.50	50.83	395.82
1.3100	1.3077	34.3	2.527	141.13	31.35	52.24	409.93
1.3176	1.3153	35.0	2.595	144.90	32.00	53.32	420.89
1.3200	1.3177	35.2	2.613	145.93	32.17	53.61	423.88
1.3300	1.3276	36.0	2.702	150.90	33.01	55.02	438.32
1.3400	1.3376	36.8	2.785	155.53	33.77	56.28	451.78
1.3500	1.3476	37.6	2.869	160.23	34.54	57.55	465.41
1.3600	1.3576	38.4	2.954	164.97	35.30	58.82	479.20
1.3678	1.3654	39.0	3.030	169.22	36.00	59.99	491.54
1.3700	1.3676	39.2	3.041	169.83	36.07	60.11	493.31
1.3800	1.3776	39.9	3.128	174.69	36.84	61.38	507.42
1.3900	1.3875	40.7	3.215	179.55	37.59	62.63	521.54
1.4000	1.3975	41.4	3.305	184.57	38.36	63.93	536.14
1.4100	1.4075	42.2	3.394	189.54	39.12	65.18	550.57
1.4200	1.4175	42.9	3.485	194.63	39.88	66.46	565.34
1.4300	1.4275	43.6	3.577	199.76	40.65	67.74	580.26
1.4400	1.4375	44.3	3.670	204.96	41.42	69.02	595.35
1.4500	1.4474	45.0	3.763	210.15	42.17	70.28	610.43
1.4600	1.4574	45.7	3.86	215.41	42.86	71.42	625.70
1.4700	1.4674	46.4	3.95	220.74	43.62	72.69	641.20
1.4800	1.4774	47.0	4.05	226.11	44.38	73.96	656.80
1.4900	1.4874	47.7	4.15	231.55	45.14	75.23	672.60
1.5000	1.4973	48.3	4.24	237.06	45.91	76.50	688.60
1.5500	1.5473	51.5	4.78	266.91	50.00	83.32	775.30

Table A4.1 Concentration of $FeCl_3$ solution in various formats

Appendix 5

Methods of analysis for free acid content in ferric chloride etching solutions

Numerous methods exist for the determination of free acid in ferric chloride etching solutions, the table over shows some of the most commonly used. Tecan have used many of the methods listed, but have found from experience that the most reliable method is the so-called 'Interconics method' developed by BMC Industries Inc, USA. This has proved suitable for both fresh and partially used etchants and is relatively straight forward to use. As with all such titration methods there is a high degree of operator skill and some variations between results are inevitable when different operators perform the same test. However other companies have found this method unreliable [Lehrer 1986]

Interconics method of analysing for free acid	
Reagents	Saturated solution of sodium thiosulphate 0.1 N solution of sodium carbonate
Method	• Dilute 5ml of ferric etching solution with 100ml of DI water • Add saturated solution of sodium thiosulphate into the solution, drop by drop, until the solution turns clear. Any further additions will cause the solution to turn brown in the flask. At this stage all of the Fe3+ will have been reduced to Fe2+ which will not precipitate out at the Ph ranges used in this titration. Adding more sodium thiosulphate will produce free hydroxide ions which will result in incorrect results from the titration. • Insert pH probe into solution and stir of 3 to 5 minuets until reading is stable. • Titrate sample with 0.1N solution of sodium carbonate. The end point is reached when the pH reading is between 4.0 and 4.1.
Calculation	$$\%HCl = \left(\frac{V_{NaOH} \times N_{Na_2CO_3} \times 36.5}{V_{FeCl_3}} \right) 100 / SG$$ Where V = Volume used N = normality ($N_{Na_2CO_3}$) SG = specific gravity of ($FeCl_3$)

iDate and Source	Complexing Agent	Neutralising Agent	Other	Indicator used?	Method of detecting neutralisation
Hays chemicals Feb 2000	Sodium thiososulphate	Sodium hydroxide		Yes	Colour change
PCMI Journal (1986)	Sodium thiososulphate	Sodium carbonate		No	pH
Hitachi Ltd Japan Analyst (1968) & PCMI Journal (1995)	Potassium oxalate	Sodium hydroxide		No	pH
Rolls Royce UK date unknown	Potassium oxalate Potassium fluoride	Sodium hydroxide	Methanol	Yes	Colour change
PCMI Journal (1986)	Potassium fluoride	Sodium hydroxide		Yes	Colour change
PCMI Journal (1987)	Potassium fluoride	Sodium hydroxide		No	pH
PCMI Journal (1987) &(1996)	Potassium fluoride	Sodium hydroxide	Methanol	No	mV swing
Unknown origin	Sodium thiososulphate	Potassium carbonate		Yes	Colour change
Berk Spencer Ltd (1984)	Ammonium sulphate	Sodium hydroxide		Yes	Colour change
PCMI Journal (1986)	Sat. Lathium chloride	Sodium hydroxide	MIBK	No	pH
Japanese Patent 10-158868 (1998)	Potassium oxalate Oxalic acid Organic acid salt	Sodium hydroxide		No	pH

Table A5.1 Typical titration methods for the determination of free acid content of ferric chloride etching solutions
[Allen, Almond and Bridges 2005]

Appendix 6

pH measurement and probes design

1. pH measurement

The pH probe used was manufactured by 'Mettler-Toledo' and was of a specific design suitable for use in acid solutions. The pH electrode is designed with a liquid electrolyte reservoir. This electrolyte is allowed to leach out of the probe tip. To facilitate this, the probe is fitted into a purpose designed housing which is pressurised to approximately 2 bar. In these tests this was initially achieved with a bicycle tyre pump but in later tests this was replaced with a compressed air supply which was found to be more reliable. Continuous outward flow of pressurized electrolyte keeps the junction free of deposits, resulting in precise and stable measurement values and prevents the ingress of ferric chloride which would destroy the electrodes. With correct maintenance, they are very well known for their long service life, even under harsh operating conditions. One probe was used continuously for a period of 16 months during this research. To accommodate the probe a special purpose housing was needed, again supplied by 'Mettler-Toledo'., as shown in Figure A6.1. Figure A6.2 shows the detail of the probe construction.

The probe, together with simpler probes for temperature and ORP monitoring were connected to a Knick 73 process unit, detailed in Appendix 7.

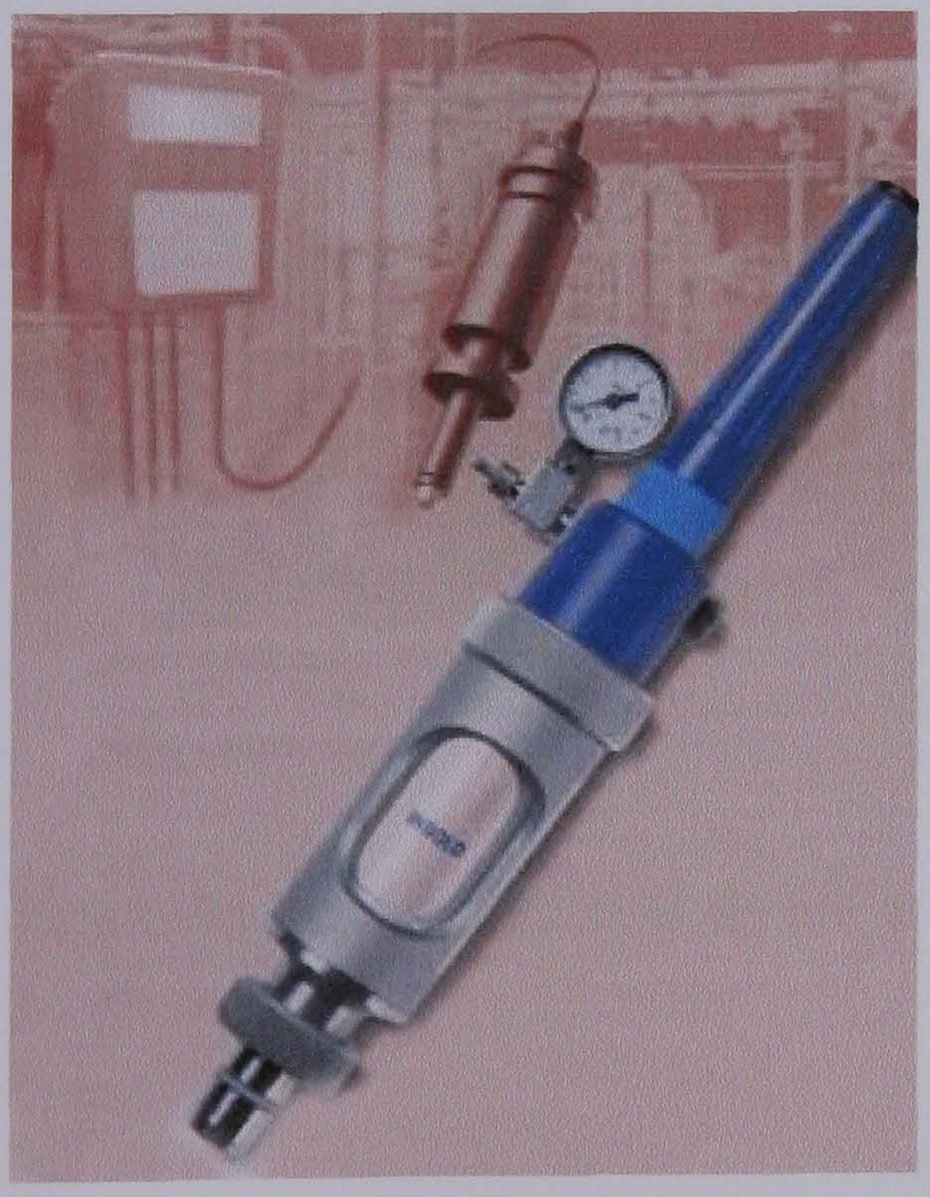


Figure A6.1

Mettler-Toledo pH probe fitted into pressurised housing.

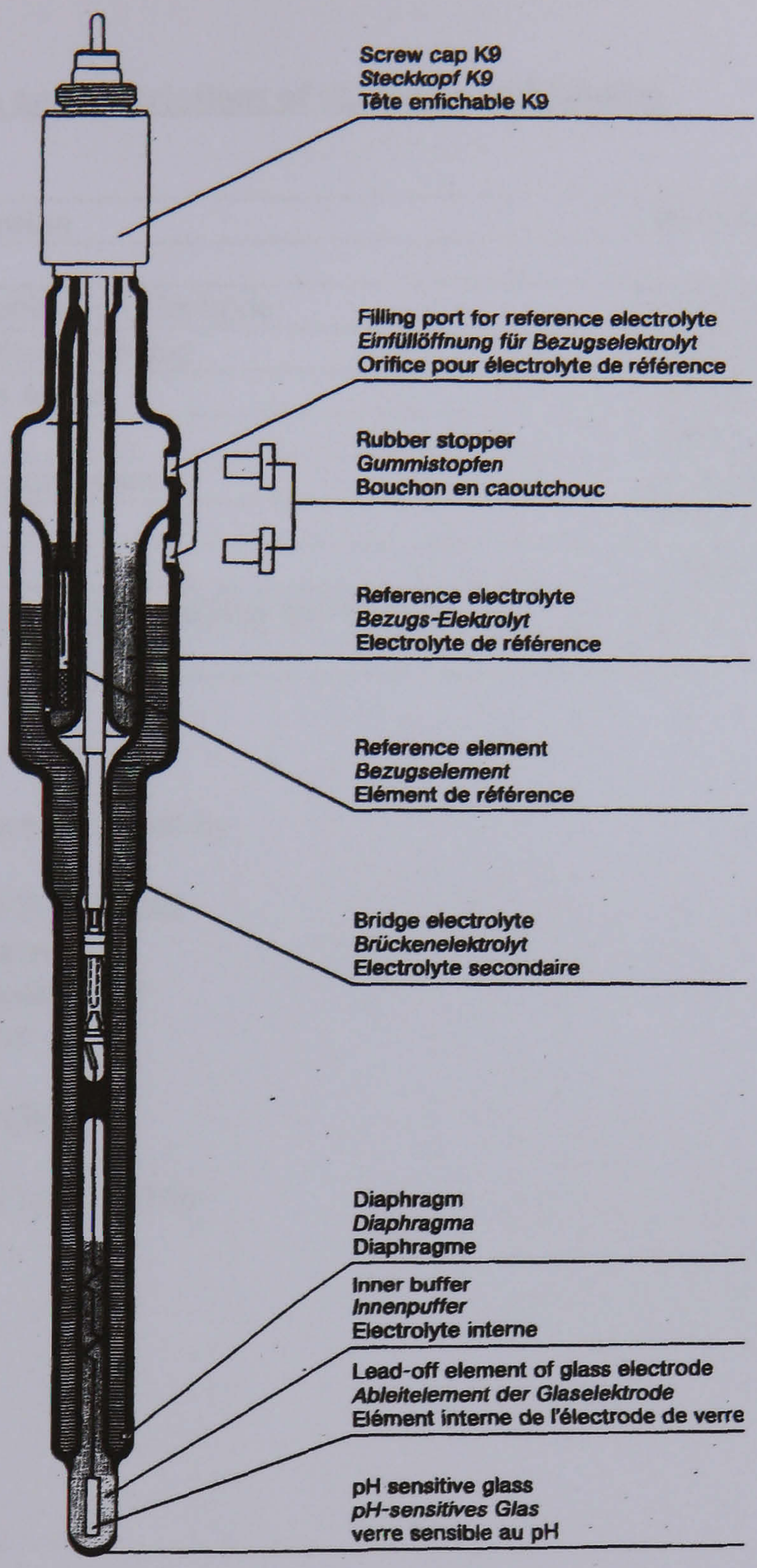


Figure A6.2 Cross section of pH probe

Part numbers and descriptions of pH probe and housing

Item	Description	Part Number
1	pH combination electrode	52001034
2	Pressurised Housing	00743189
3	Weld in socket	007641223
4	Cable	100010502
5	Temperature sensor	1010032072
6	Cable	100011002
7	Socket	52400252
8	Wall mounted transmitter and display	52121108

All the above was supplied by

Mettler Toledo Ltd
64 Boston Road
Beaumount Leys
Leicester
UK
LE4 1AW

Tel : 0116 235 6706

Appendix 7

Details of equipment used during research

Etching machine

Chemcut etching machine with a sump capacity of 450 litres fitted with a hydrometer for the measurement of density in °Bé.

The above items were supplied by

Chemcut Corporation
State College,
Pennsylvania, USA

pH meter

Knick Process Unit 73 pH meter, pH, ORP and temperature electrodes. A full description of this probe is given in appendix 6. All items were supplied by

Elscolab B.V.
Zonnebaan 18- 18
3606 CB MAARSSENBROEK

http://www.knick.de

Figure A7.1 Knick controller used to measure pH, ORP and temperature

Oxygen delivery and measuring equipment

Oxygen gas flow meter with a measurement range of 40-400 litre/minute.

The above items were supplied by

Platon Instrumentation
Jays Close, Viables,
Basingstoke, Hampshire RG22 4BS

Oxygen delivery equipment (control valves, regulators etc.) supplied by

Air Products
Hampshire International Business Park
Crockford Lane
Chineham
Basingstoke, Hampshire, RG24 8GA

Static Mixer

The above item was supplied by

Koch Engineering Company, Inc.
P.O. Box 8127
Wichita, Kansas
USA

Figure A7.2 Typical static mixer

The model used was 50mm diameter, 500mm long with fixed mixing elements arranged in 9 section each rotated at 90° to the previous section. The construction was entirely polypropylene to allow it to survive the ferric chloride etchant.

HCl Dosing Pump

Gamma series 4, diaphragm pump supplied by

ProMinent Fluid Controls (UK) Ltd.
Resolution Road
Ashby de la Zouch
Leicestershire, LE65 1DW

http: www.prominent.co.uk

Figure A7.3 HCl dosing pump – Gamme series 4

Circulation Pump

Make and model

Finish Thompson KC11 360 l/min @1.8 bar

Supplied by

Michel Smith Engineers Ltd.
Oaks Road
Woking, Surrey, UK GU21 6PH

http://www.michael-smith-engineers.co.uk

Conductivity meter and probe

Measurement of conductivity was achieved using a Walchem WEC conductivity controller and PEEK 316SS toroidal electrodless probe, both are standard industrial instruments and were supplied by Semat Technical Ltd. Figures A7.4 and A7.5 shows the probe and meter used.

Semat Technical (UK) Ltd.
One Executive Park
Hatfiled Road
St. Albans
Herts, AL1 4TA

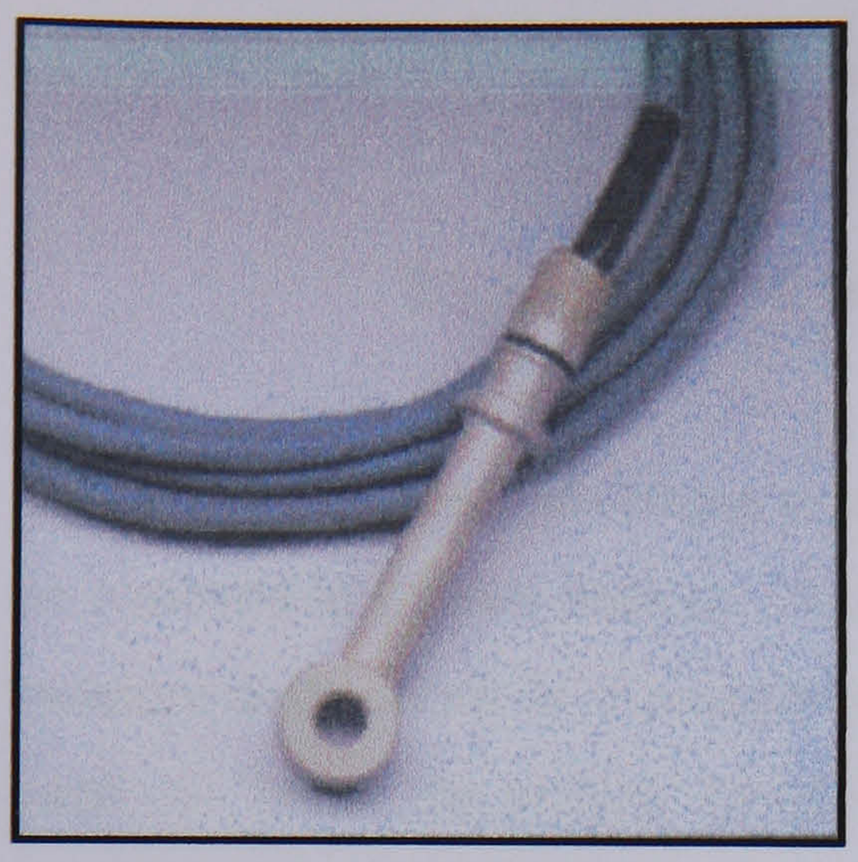


Fig A7.4 Peek 316SS conductivity probe

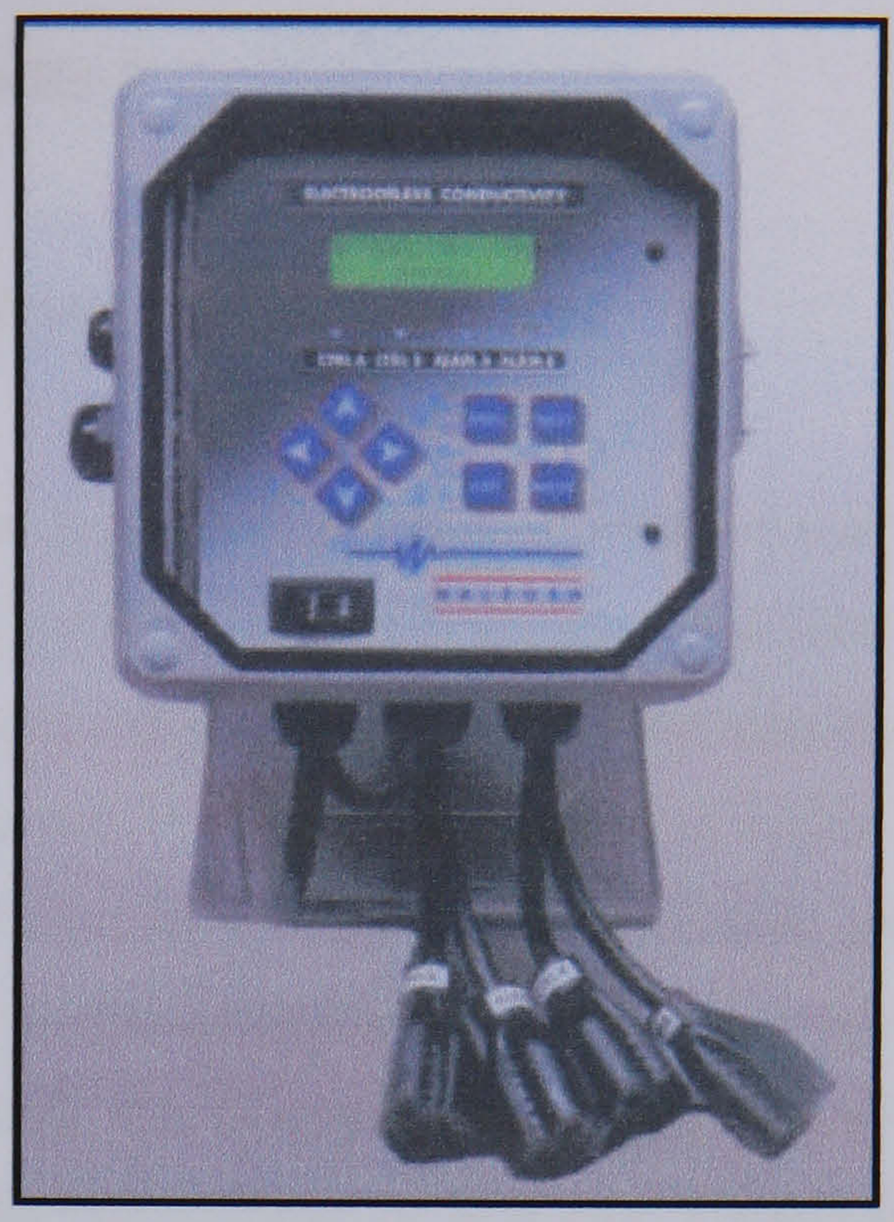


Figure A7.5 WEC Conductivity controller used to display conductivity and transmit data to data collection

Device net items

The following is a list of items used in the data capture, transfer and storage.

Item	Description	Part Number	Qty
1	4 – 20 mil V interface module	1734 – IE2L	2
2	Switch relay module	1734 – OW2	2
3	Device net interface module	1734 – PDN	1
4	Device net cable	1734 – CBW	500 m
5	Device net interface module	1756 – DNB	1
6	Ethernet interface module	1756 – 1	1
7	Power supply	1786 – 2	1
8	Software	RS View 32	

All the device net monitoring equipment and software was purchased from

Rockwell Automation Ltd
Pitfield, Kiln Farm
Milton Keynes
MK11 3DR
United Kingdom
www.rockwellautomation.com/support

Appendix 8

Etching speed calculations and conversions

Traditionally the rate of etching is expressed in terms of the amount of metal that can be removed in a given time i.e. 25 microns per minute. This is sometimes difficult to measure and control in a production environment so other measures are commonly used. At Tecan the etching speed is expressed in terms of the speed at which the machine runs to achieve a given depth of etch in a single pass (metal only going through the machine once).This measure is further simplified at Tecan by expressing the speed not in actual units i.e. cm per minute, but in terms of the dial setting of the machine. The charts below give some useful comparisons of etch sped expressed in various ways. The last chart shows the typical degradation which is seen in metal removal rates as etchant ages without regeneration.

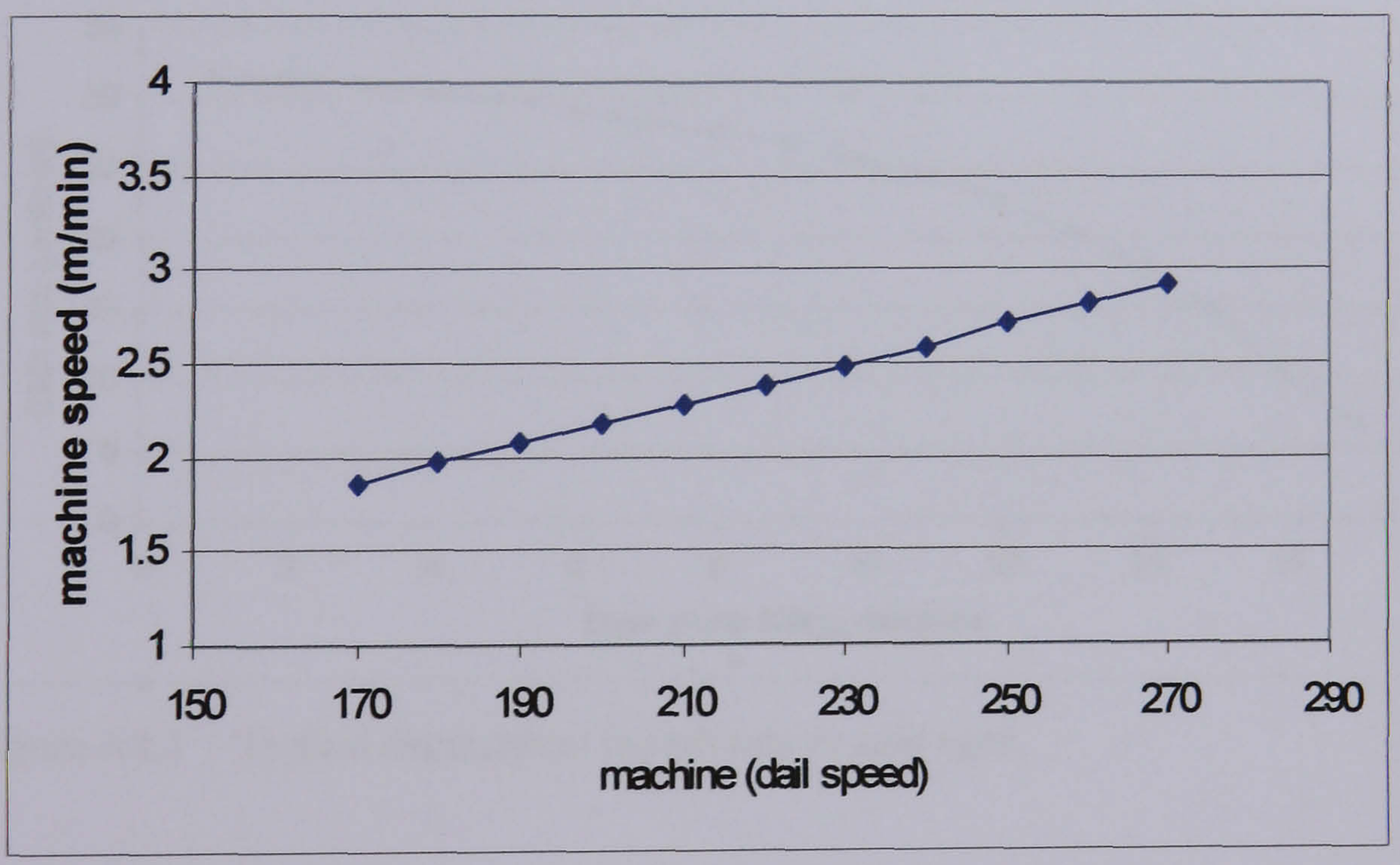


Figure A8.1 Etch speed expressed in terms of machine dial setting and machine governor speed.

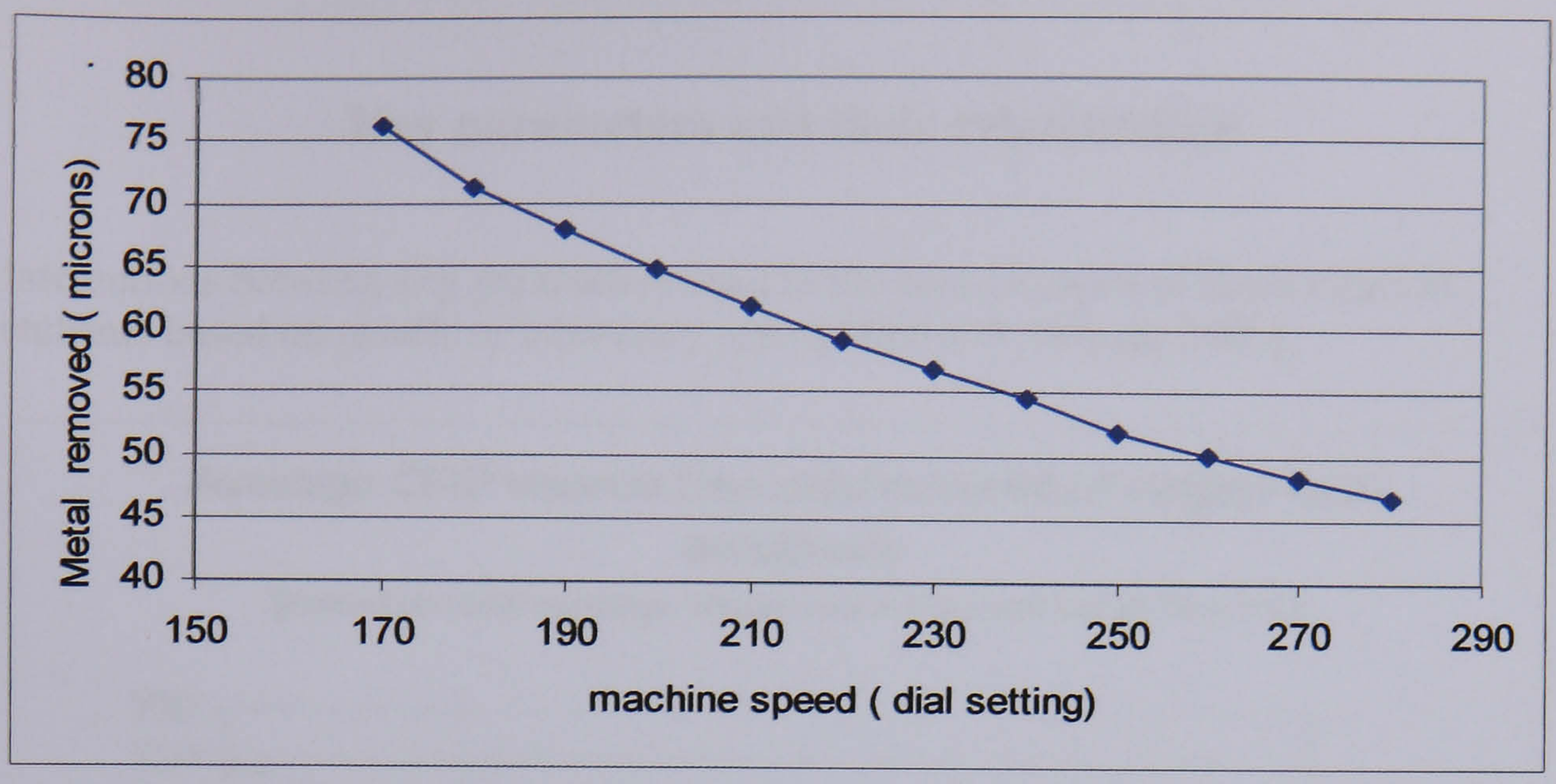


Figure A8.2 Etch speed expressed in terms of machine dial setting and depth of etch.

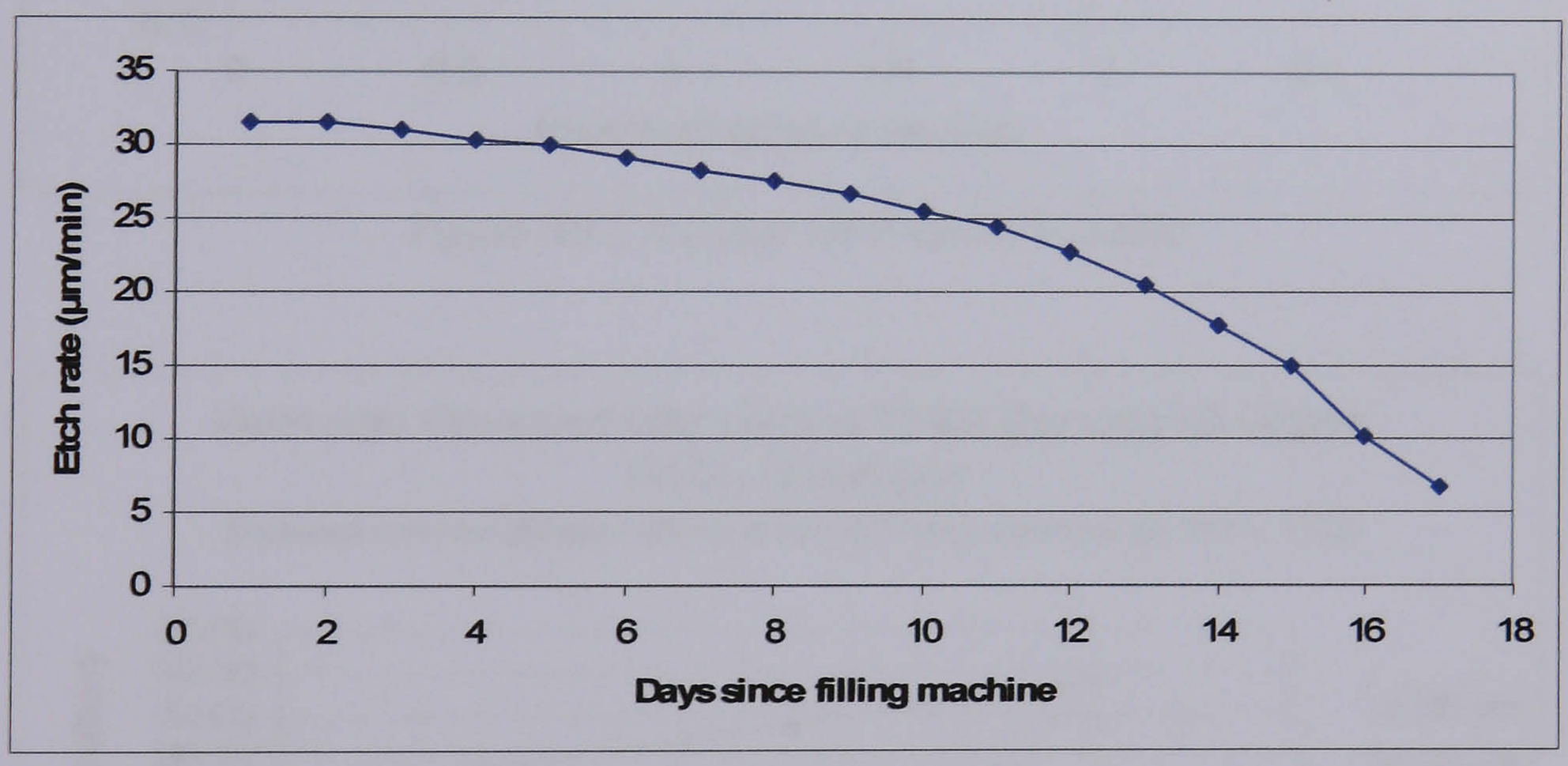


Figure A8.3 Typical degradation in etch rate as acid ages.

Appendix 9

Key parameters and their relationships

Interactions between key parameters used in the measurement of ferric chloride etchants based on results of laboratory tests [Allen and Almond 2005]

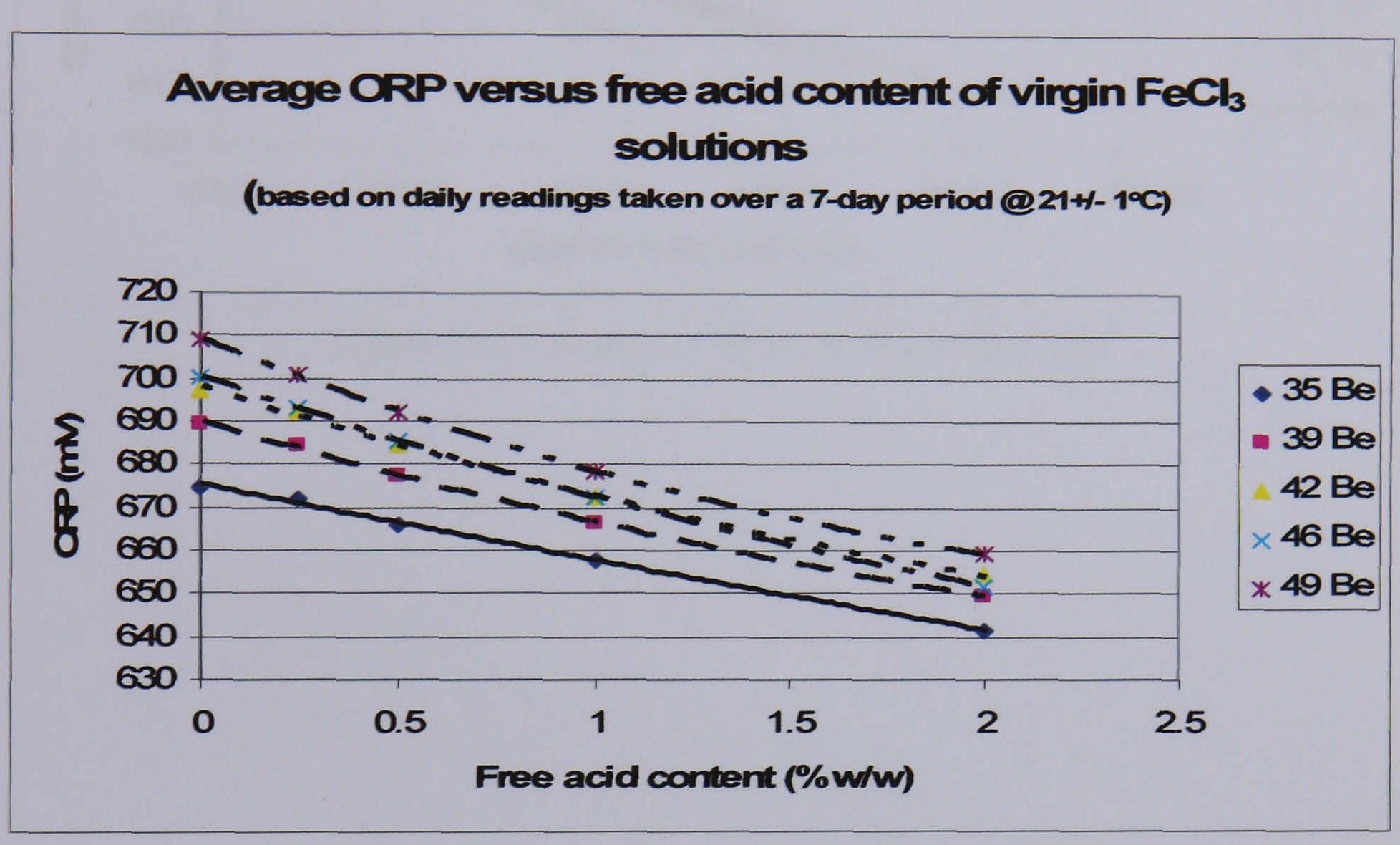


Figure A9.1 Average ORP verses free acid

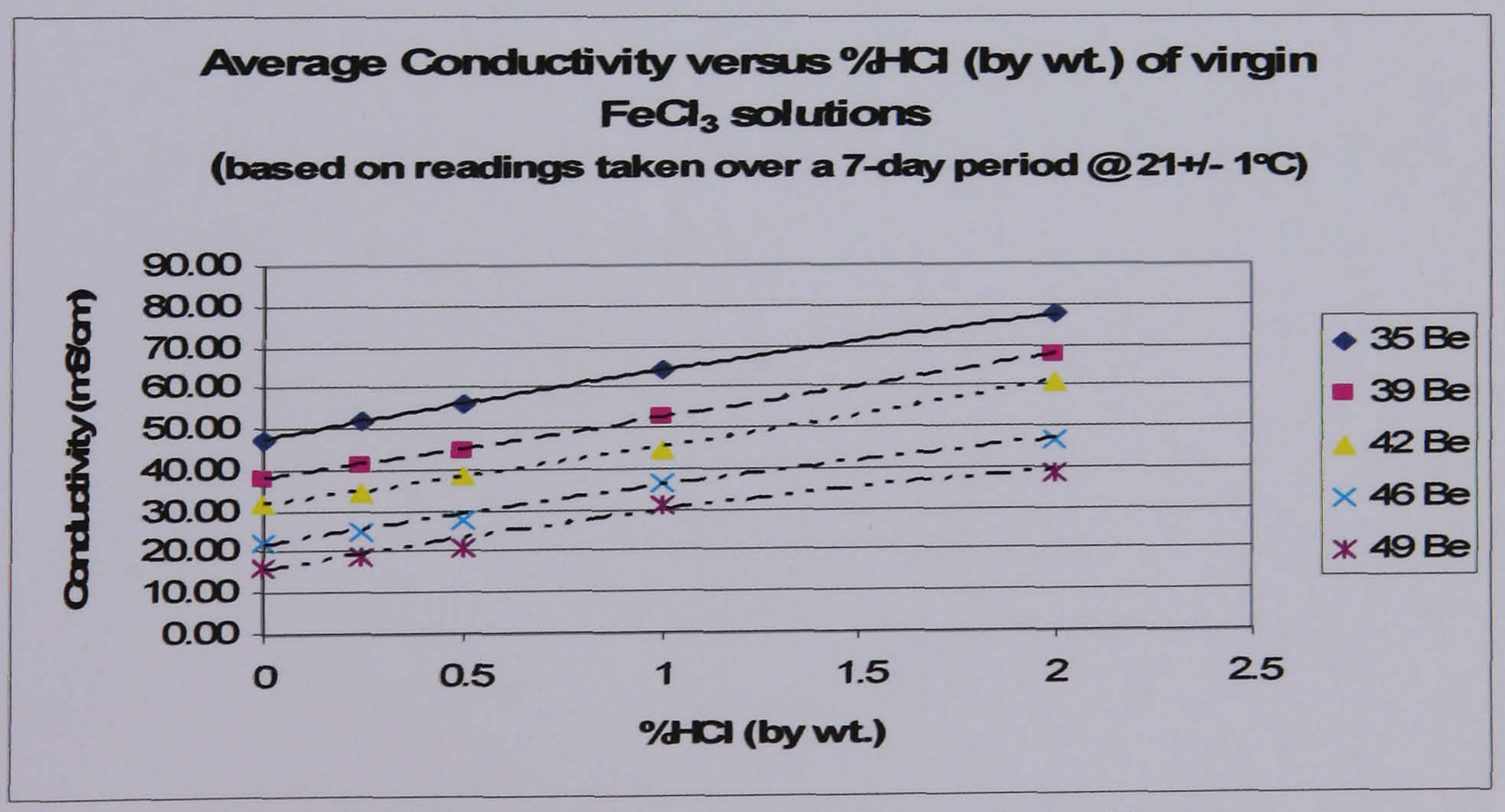


Figure A9.2 Average conductivity verses free acid content

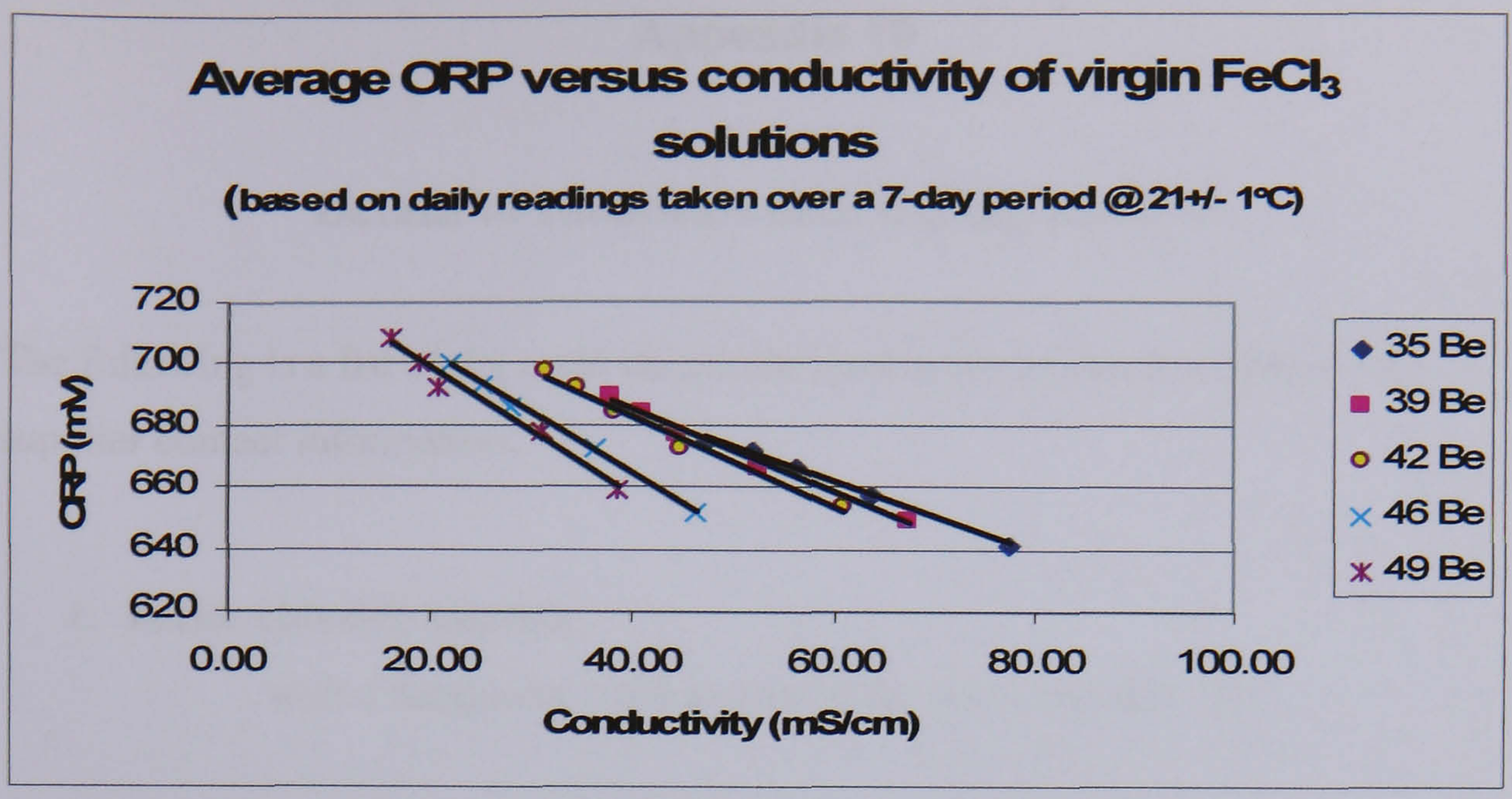


Figure A9.3 Average ORO verses conductivity

Appendix 10

Details of chemicals used during research

The following is a list of the main chemicals used in this research together with supplier contact information.

1. **Ferric chloride solution**,

   with a maximum 0.6% hydrochloric acid content.42 °Bé.

2. **Hydrochloric acid** (concentrated, 32% volume/weight)

The above items were supplied by

Hays Chemicals Distribution Ltd.

Cogdean Elms Works,

Higher Merley Lane,

Corfe Mullen

Wimbourne, Dorset BH21 3EH

3. **Compressed oxygen** and related fittings such as regulators and flashback arrestor. The oxygen gas was supplied in a cylinder and at a minimum concentration of 99.4% purity. Each cylinder occupies a capacity of 10.05 m^3 at standard temperature and pressure.

The above item were supplied by

Air Products plc

Hampshire international Business Park,

Crockford Lane, Chineham

Basingstoke, Hampshire RG24 8GA

Appendix 11

Sample of data

The following table is a small example of the typical data used to monitor and analysis the ferric chloride etching solution. In total over 80Mb of data was captured and summarised during this study. This data is derived from the output from the data collection and storage system detailed in section 4.3

Date	Time	COND	ORP	PH	TEMP	T1	T2
09/11/2004	04:37:35	27.30000	576.00	-0.570	46.60000	0	0
09/11/2004	04:42:35	27.20000	576.00	-0.570	46.50000	0	0
09/11/2004	04:47:35	27.70000	576.00	-0.560	46.70000	0	0
09/11/2004	04:52:35	27.30000	576.00	-0.570	47.10000	0	0
09/11/2004	04:57:36	27.30000	576.00	-0.570	46.70000	0	0
09/11/2004	05:02:36	27.20000	576.00	-0.570	46.50000	0	0
09/11/2004	05:07:36	27.30000	575.00	-0.570	46.40000	0	0
09/11/2004	05:12:36	27.90000	576.00	-0.560	47.10000	0	0
09/11/2004	05:17:36	27.40000	576.00	-0.570	47.00000	0	0
09/11/2004	05:22:36	27.20000	576.00	-0.570	46.70000	0	0
09/11/2004	05:27:36	27.20000	576.00	-0.580	46.50000	0	0
09/11/2004	05:32:36	27.30000	576.00	-0.570	46.40000	0	0
09/11/2004	05:37:36	27.80000	576.00	-0.560	46.90000	0	0
09/11/2004	05:42:36	27.30000	576.00	-0.570	47.00000	0	0
09/11/2004	05:47:36	27.30000	576.00	-0.570	46.60000	0	0
09/11/2004	05:52:36	27.10000	576.00	-0.580	46.50000	0	0
09/11/2004	05:57:36	27.70000	576.00	-0.560	46.60000	0	0
09/11/2004	06:02:36	27.40000	576.00	-0.570	47.10000	0	0
09/11/2004	06:07:36	27.30000	576.00	-0.580	46.70000	0	0
09/11/2004	06:12:36	27.20000	576.00	-0.580	46.50000	0	0
09/11/2004	06:17:36	27.50000	575.00	-0.570	46.50000	0	0
09/11/2004	06:22:36	27.60000	576.00	-0.560	47.20000	0	0
09/11/2004	06:27:36	27.30000	576.00	-0.570	46.90000	0	0
09/11/2004	06:37:36	27.20000	576.00	-0.580	46.40000	0	0
09/11/2004	06:42:36	27.70000	576.00	-0.560	46.70000	0	0
09/11/2004	06:47:36	27.30000	576.00	-0.570	47.10000	0	0
09/11/2004	06:57:36	27.10000	576.00	-0.570	46.50000	0	0
09/11/2004	07:02:36	27.30000	575.00	-0.570	46.30000	0	0
09/11/2004	07:07:36	27.60000	576.00	-0.560	47.00000	0	0

Table A11.1 Typical date capture date

Key to column headings

DATE and TIME – system time indicating the point at which the data was captured

COND – conductivity measured in mS/cm

ORP – the solution ORP value

PH – the solution pH

TEMP – the temperature of the solution on Deg C

T1 and T2– flag showing the status of the mixing and dosing pumps

The chart below is taken from the data above (only part of raw data for this day is shown in table for clarity) and is typical of the type of output generated from the data capture and used in the analysis of the experimental research.

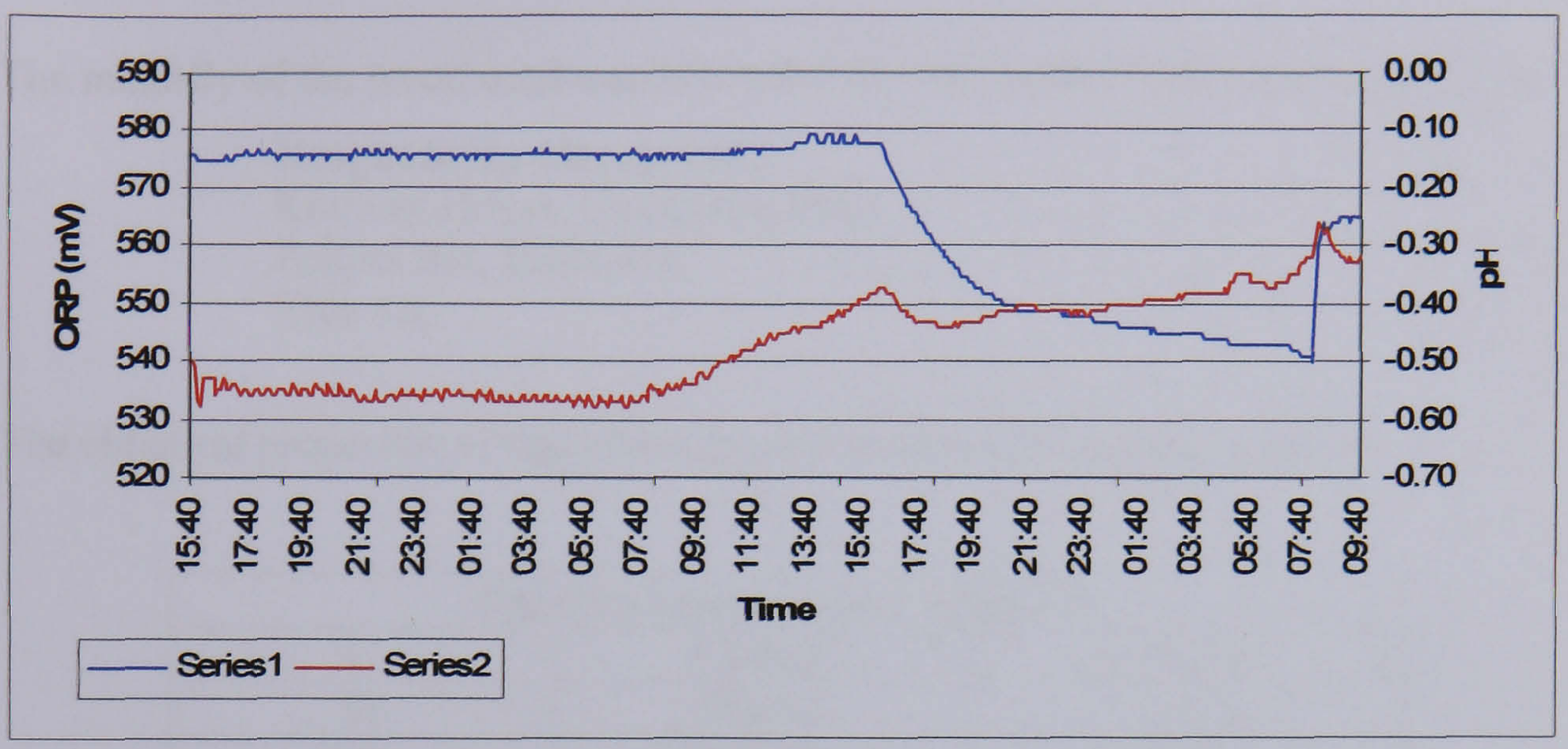


Figure A11.1 typical chart from data capture system

Appendix 12

Details of metal used during the experimental work

The majority of the metal used was BS1449 PT2 1983 **430**S17, this was supplied by

Knight Strip Metals Ltd,
Knuway House, Cranborne Road
Potters Bar, Herts, UK
EN6 3JL

The chemical properties of this particular specification of stainless steel are:-

Chemical composition weight %		
C	Carbon	≤ 0.12
Si	Silicon	≤ 1.0
Mn	Manganese	≤ 1.0
P	Phosphorus	≤ 0.040
S	Sulphur	≤ 0.030
Cr	Chromium	16.0 to 18.0
Ni	Nickel	≤ 0.75
Mo	Molybdenum	≤ 0.50
Cu	Copper	≤ 0.50
N	Nitrogen	0
Fe	Iron	Bal

As this was a production machine, on occasions other materials were etched; mainly BS5779 PT4 1981 **302**S25 grade stainless steel. This grade of stainless steel differs from 430 mainly in the quantity of nickel present 302 has between 8 and 10%. nickel. It is not felt that this would have significantly influenced the results. Only small quantities of material would have been dissolved into the etchant.

Pure nickel which had been produced by the electroforming process was also etched. It is not felt that this would have had any adverse effect on the results since only very small amounts of nickel were removed from the blanks. It is estimated that during the extended oxygen regeneration tests only 7kg in total of pure nickel was etched into solution.

Appendix 13

Etching machine control sheet

Week start date *9 May 2005*

	Machine records				
	Baume	Temp °C	Qty. of blanks	Etch Speed	Additions (ltrs)
Mon	*40*	*55*	*51*	*230*	*10 H_2O*
Tue	*39*	*55*	*46*	*230*	
Wed	*39*	*55*	*28*	*230*	*10 H_2O*
Thu	*39*	*55*	*27*	*230*	
Fri	*39*	*55*	*22*	*230*	*35 HCl*
Sat					
Sun					

	Average date from system			
	Free acid	Cond.	ORP	pH
Mon		*36.7*	*548*	*-0.69*
Tue		*37.6*	*550*	*-0.54*
Wed		*37.0*	*550*	*-0.51*
Thu		*39.1*	*543*	*-0.61*
Fri		*37.6*	*544*	*-0.49*
Sat				
Sun				

Comments

Good clean etch – no smut

NB (This table was transcribed from the actual date recorded for this period)

Appendix 14

Calculation of chemical additions for oxygen regeneration

Atomic weights

From tables

Iron (Fe)	55.85
Chlorine (Cl)	35.45
Oxygen (O)	16
Hydrogen (H)	1

Molecular weights (by calculation)

Hydrochloric acid	36.45
Ferrous chloride	126.75

Cycle of regeneration

Ferric chloride $8FeCl_3$

During etching – (iron) $4Fe + 8FeCl_3$

Resulting in Ferrous chloride $12FeCl_2$

Regeneration with oxygen $3O_2 + 12HCl + 12FeCl_2$

Fresh ferric $12FeCl_3 + 6H_2O$

Using the equations and atomic weight above the following can be calculated

Total reaction $3O_2 + 12HCl + 12FeCl_2 \rightarrow 12FeCl_3$

Therefore, using the molecular weights, to regenerate 126.6 grams of ferrous chloride, 8 grams of oxygen and 36.5 grams of HCl will be required, were both the oxygen and HCl values are expressed as gas.

Appendix 15

Calculations of the saving made when using oxygen regeneration

The following show the calculation for savings when using oxygen regeneration compared etching without regeneration. Based on 500kg of metal removed per year.

Equipment cost			**Notes**
	ORP and pH probe, housing and cables	£1,318.00	
	pH meter	£ 520.00	
	Monitoring equipment	£1,700.00	
	Sampling loop	£ 90.00	
	HCL pump	£ 220.00	
	Total	£3,848.00	
	Cost per year	£ 769.60	*[1]*
Chemical cost			
	Average cost of HCl	£ 9.00	*[2]*
	Average cost of Ferric chloride additions	£ 6.87	*[3]*
	Total cost per year	£ 793.50	*[4]*
Total cost per year		£1,563.10	
Savings			
	Ferric chloride (@ 0.275p/ltr)	£3,080.00	*[5]*
	Labour (@ £12/hr)	£ 672.00	*[6]*
	Waste chemistry (@ 0.45p/ltr)	£5,040.00	*[5]*
Total savings per year		£8,792.00	
	Net saving per year	**£7,228.90**	

Based on the following assumptions

[1] Based on typical 5 year payback
[2] 35 ltr/wk at 0.257 p/ltr
[3] 25 ltr/wk at 0.275 p/ltr
[4] Based on 50 working weeks per year
[5] Assuming replacement required every 3.5 weeks
[6] Based on 4 hours to complete change of chemistry in etching machine

Appendix 16

Selection of charts from experimental work

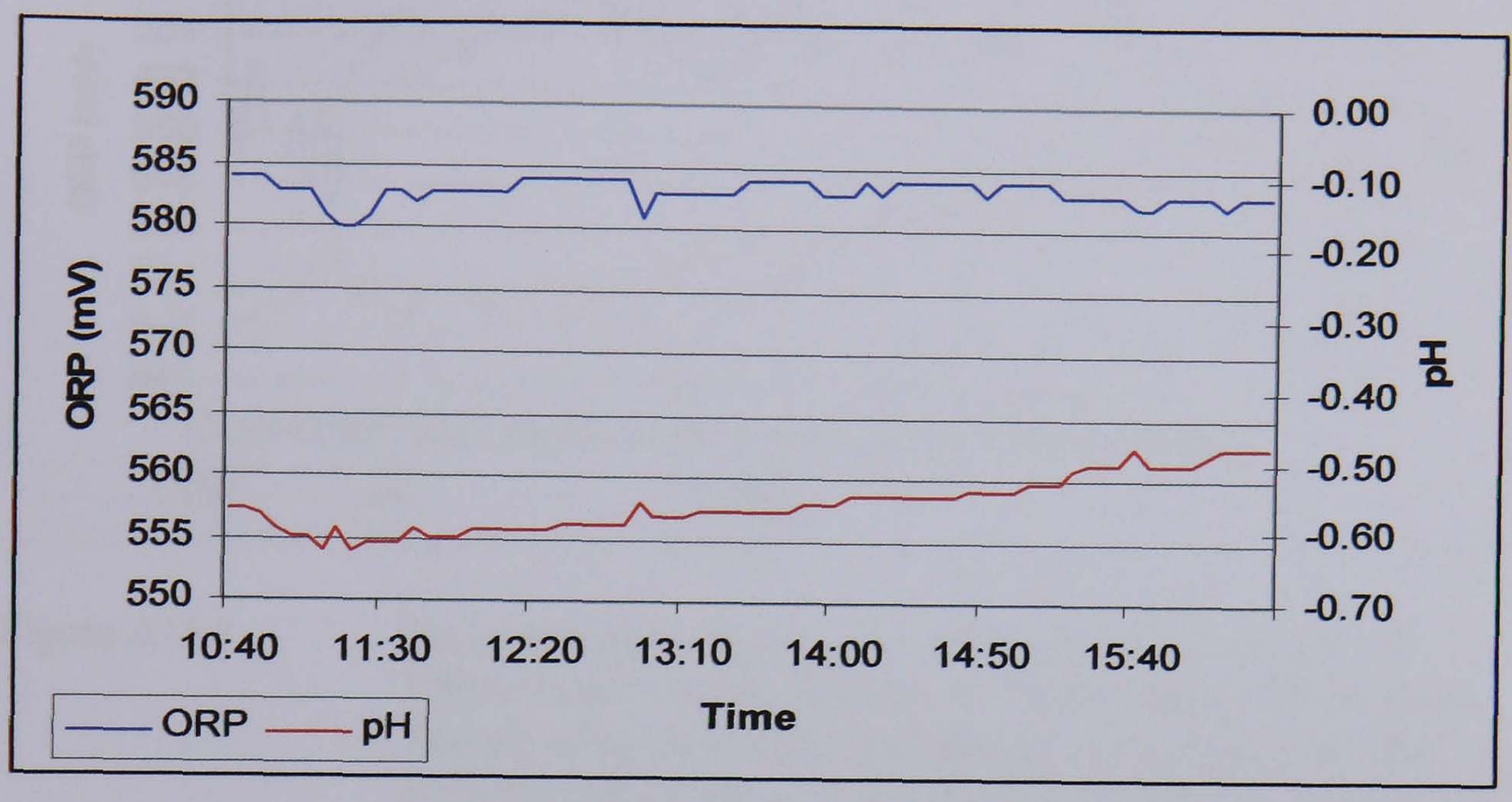


Figure A16.1 Early oxygen regeneration test – oxygen flow rate 4 ltr/min HCl flow rate 25ml/min – no regeneration and free acid rising as it is used up by etching proves *(test date 13/4/04)*

Figure A16.2 Early static mixer test, flow rate of Oxygen 10 ltr/min and HCl 50 ml/min, no regeneration observed *(Test date 22/4/05)*

Figure A16.3 Horizontal static mixer test, using oxygen at flow rate of 10ltr/min and HCl at 5ml/min, not controlled by pH set point. Test showing ph rising overnight but no regeneration, raise probably due to free acid driven off by tempt – no acid control at this point. *(Test date 8/7//04)*

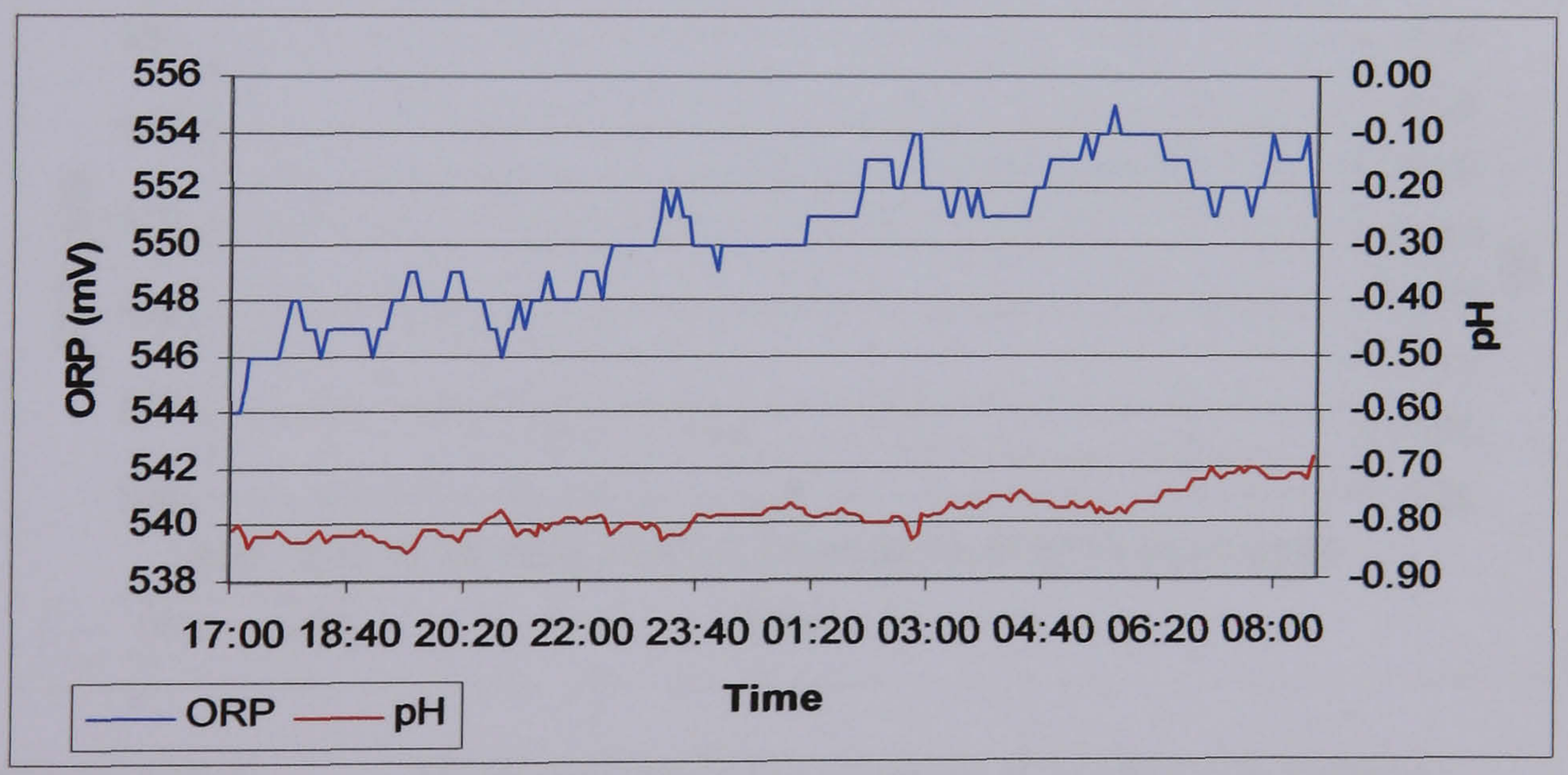


Figure A16.4 Overnight spray test – pH held stable by control system ORP increasing during test due to regeneration. Note some rise in pH at start of working day as etching commenced.
(Test date 20/9/04)

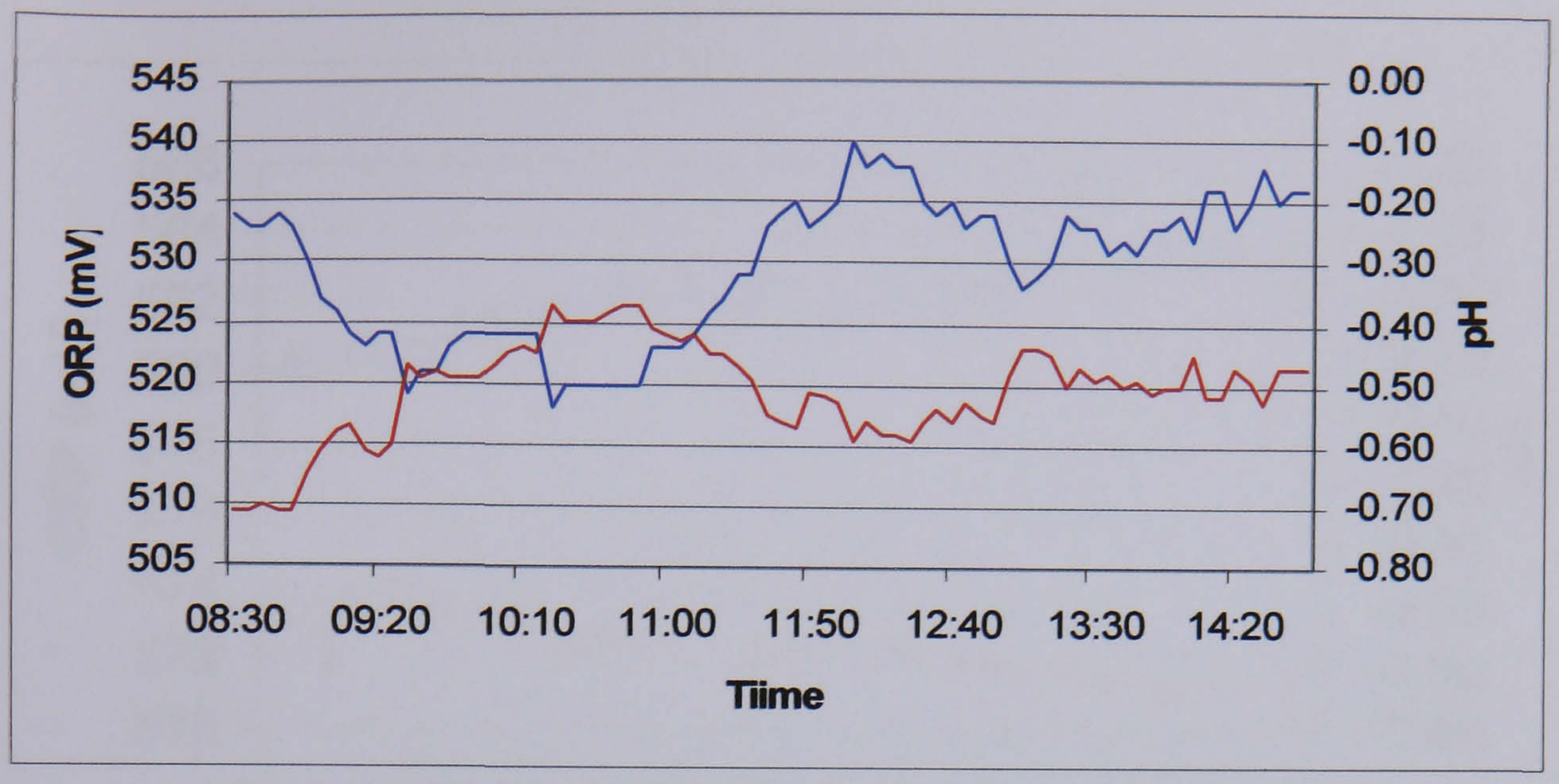


Figure A16.5 Showing how free acid and ORP fall until 11:00 when control switched on pH falls to set point ORP increases *(Test date 05/10/04)*

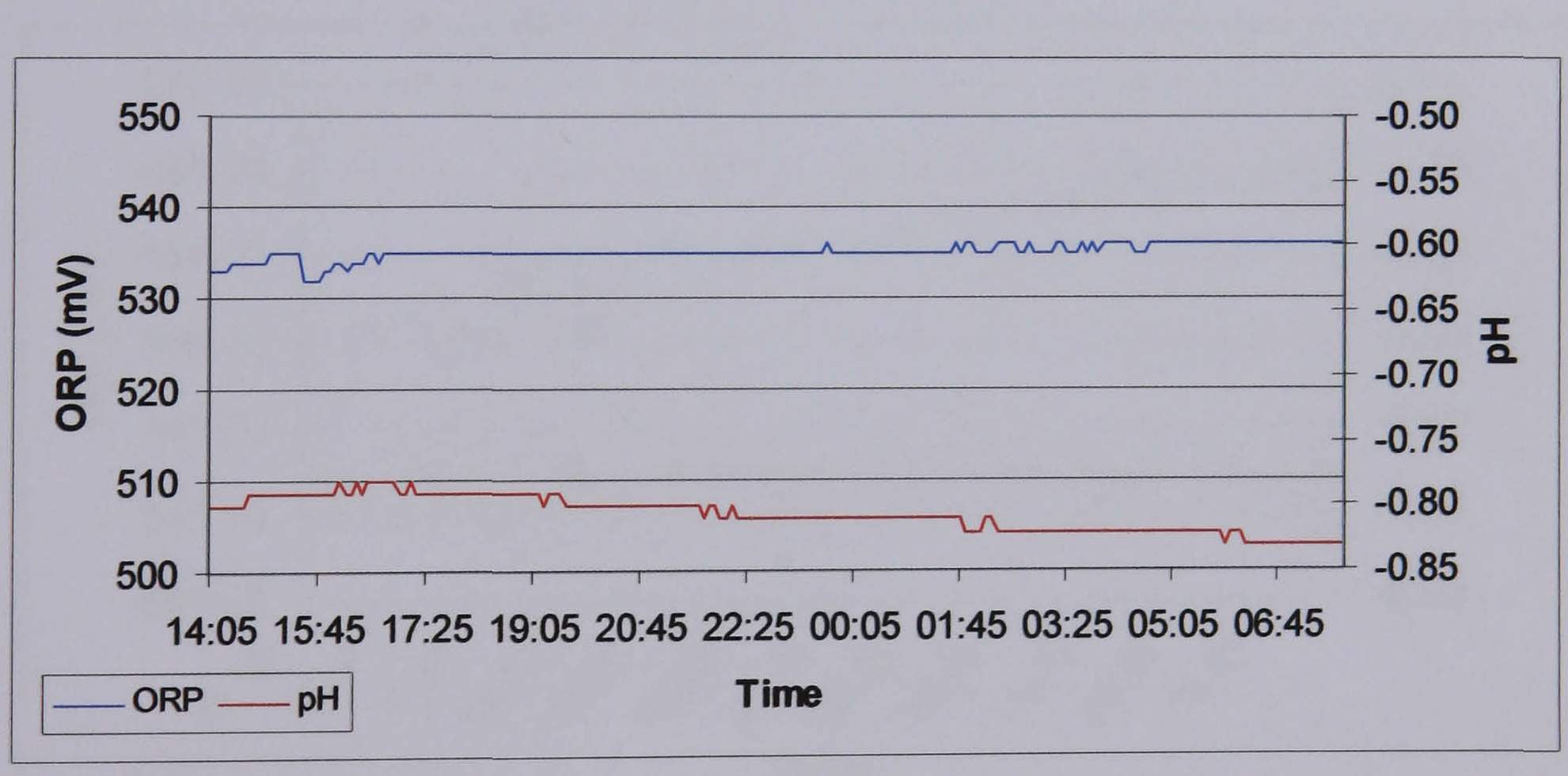


Figure A16.6 Horizontal mixer test overnight using air (10ltr/min), no regeneration *(Test date 12/10/04)*

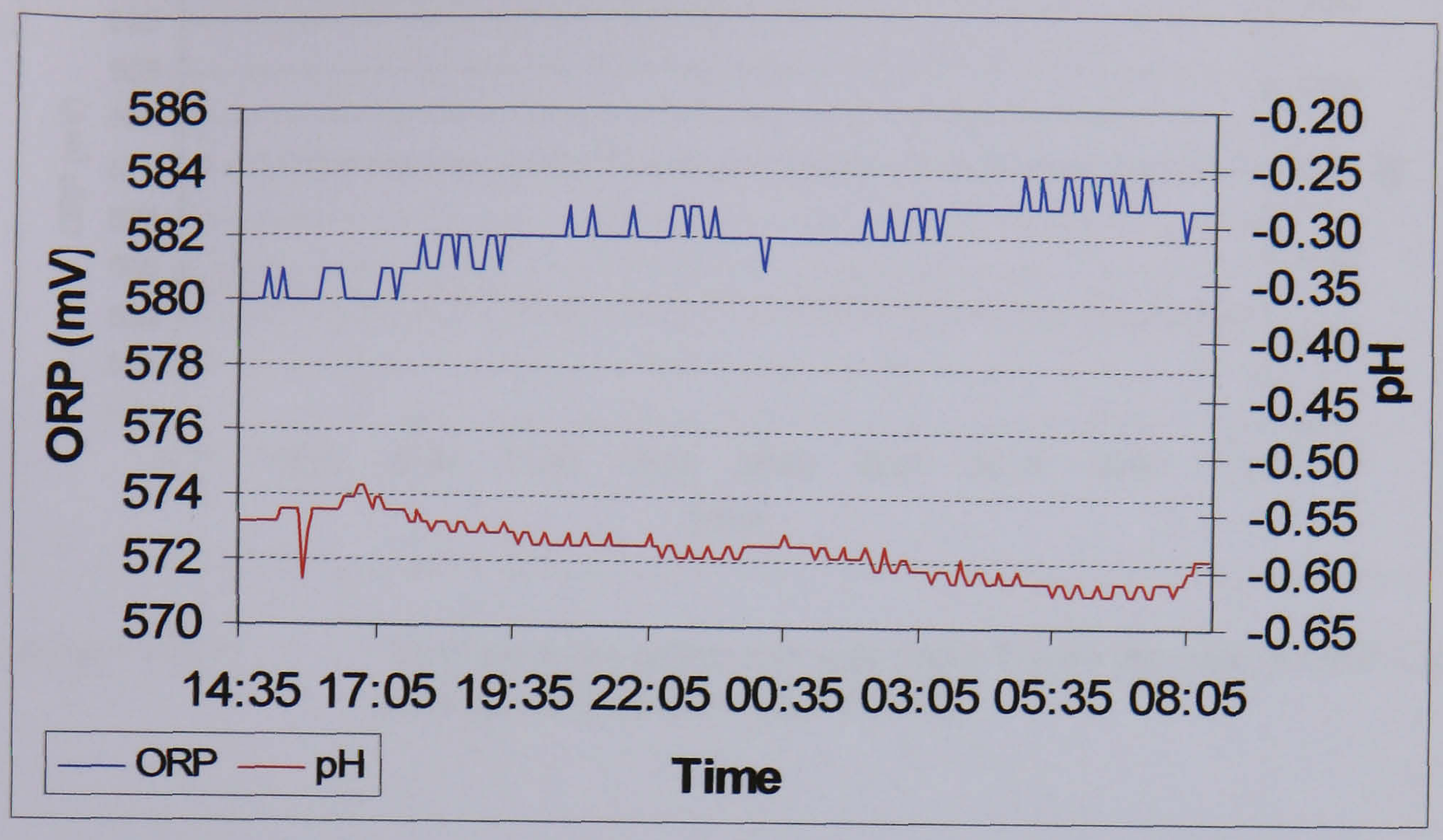


Figure A16.7 Overnight regeneration test with controlled pH, ORP increasing, OR increase not as large as expected but would have been suppressed by fall in pH. *(Test date 4/11/04)*

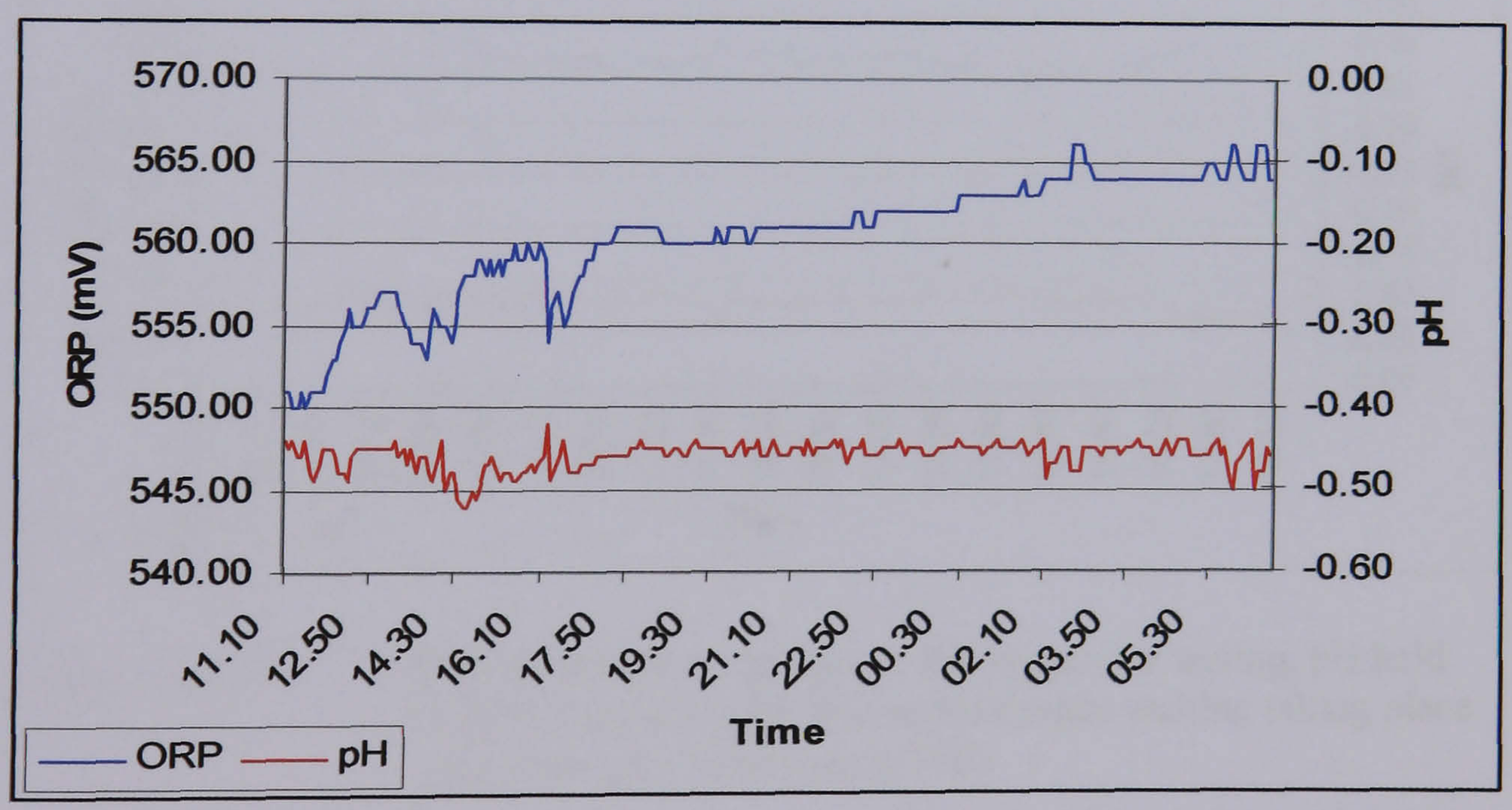


Figure A16.8 Extended spray test, static pH, some increase in ORP indicating regeneration. Note changes in both ORP and pH during normal operation when material was being etched, this stablised overnight. *(Test date 23/11/04)*

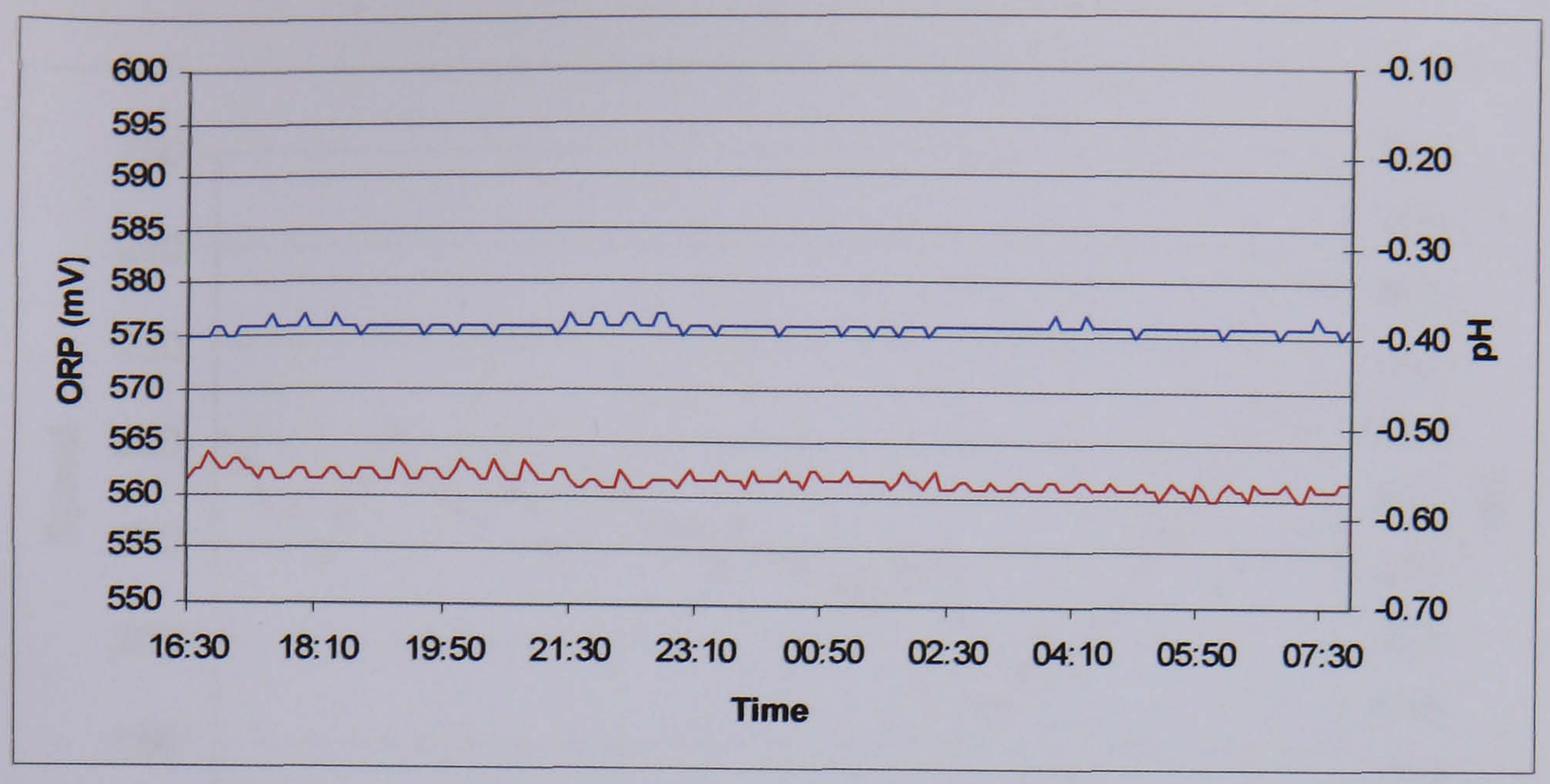


Figure A16.9 Vertical static mixer test –pH stable but no increase in ORP, i.e. no regeneration *(Test date 16/3/05)*

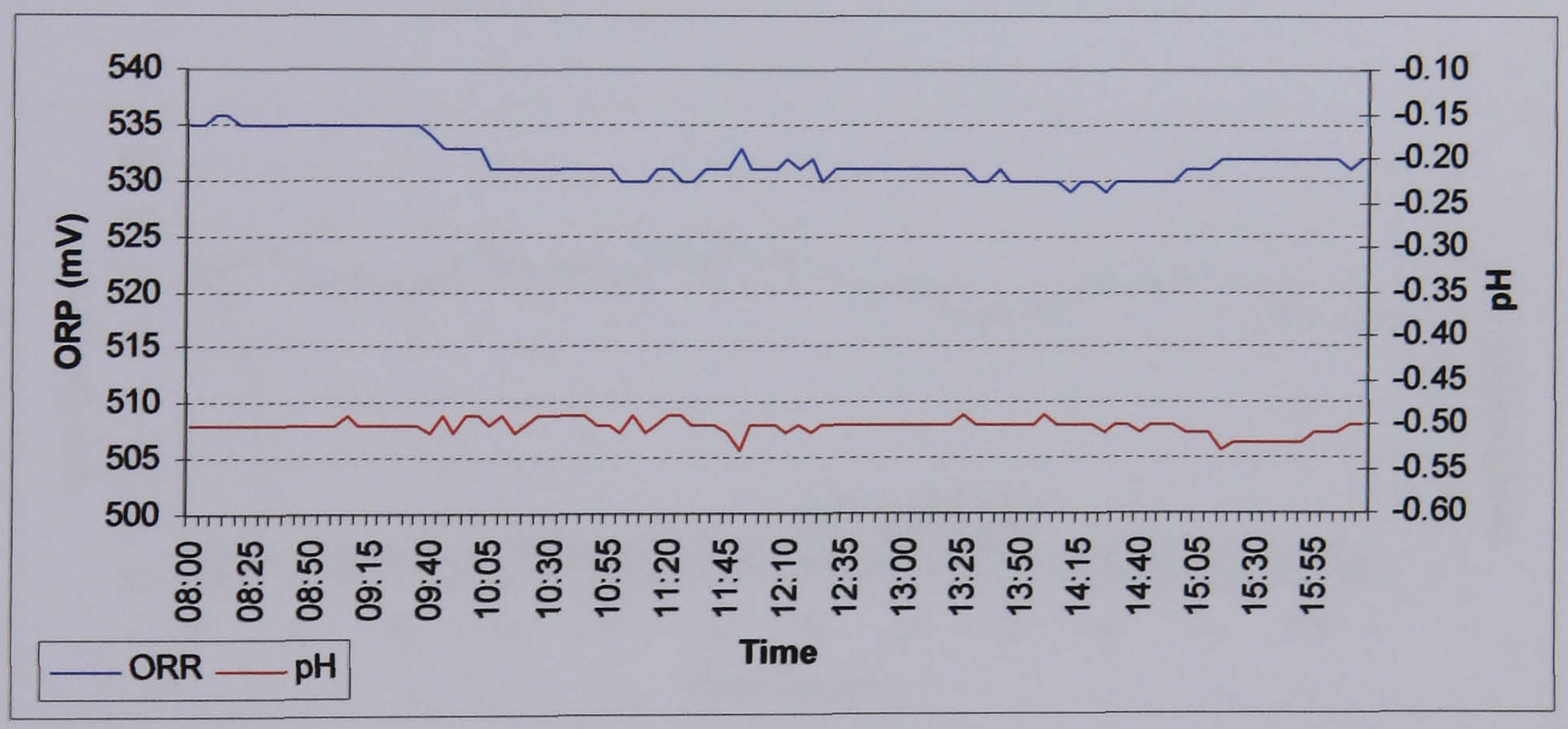


Figure A16.10 Typical data from the end of the oxygen/air testing, pH held stable by system ORP also stable despite etching taking place during the day. *(Test date 4/5/05)*

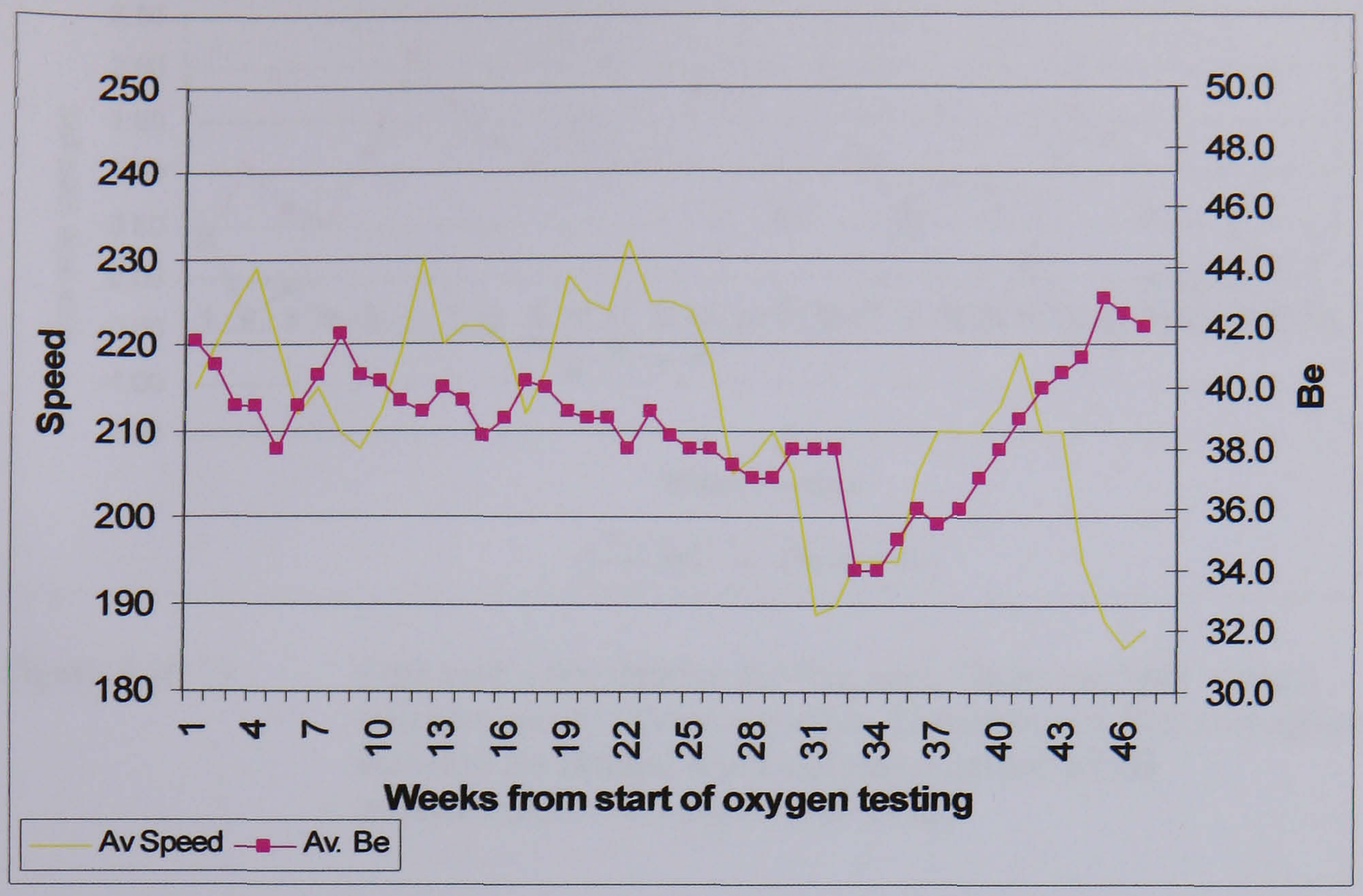


Figure A16.11 Etch speed plotted against Baumé of the etchant for extend regeneration tests *(Test started Jan 2005)*

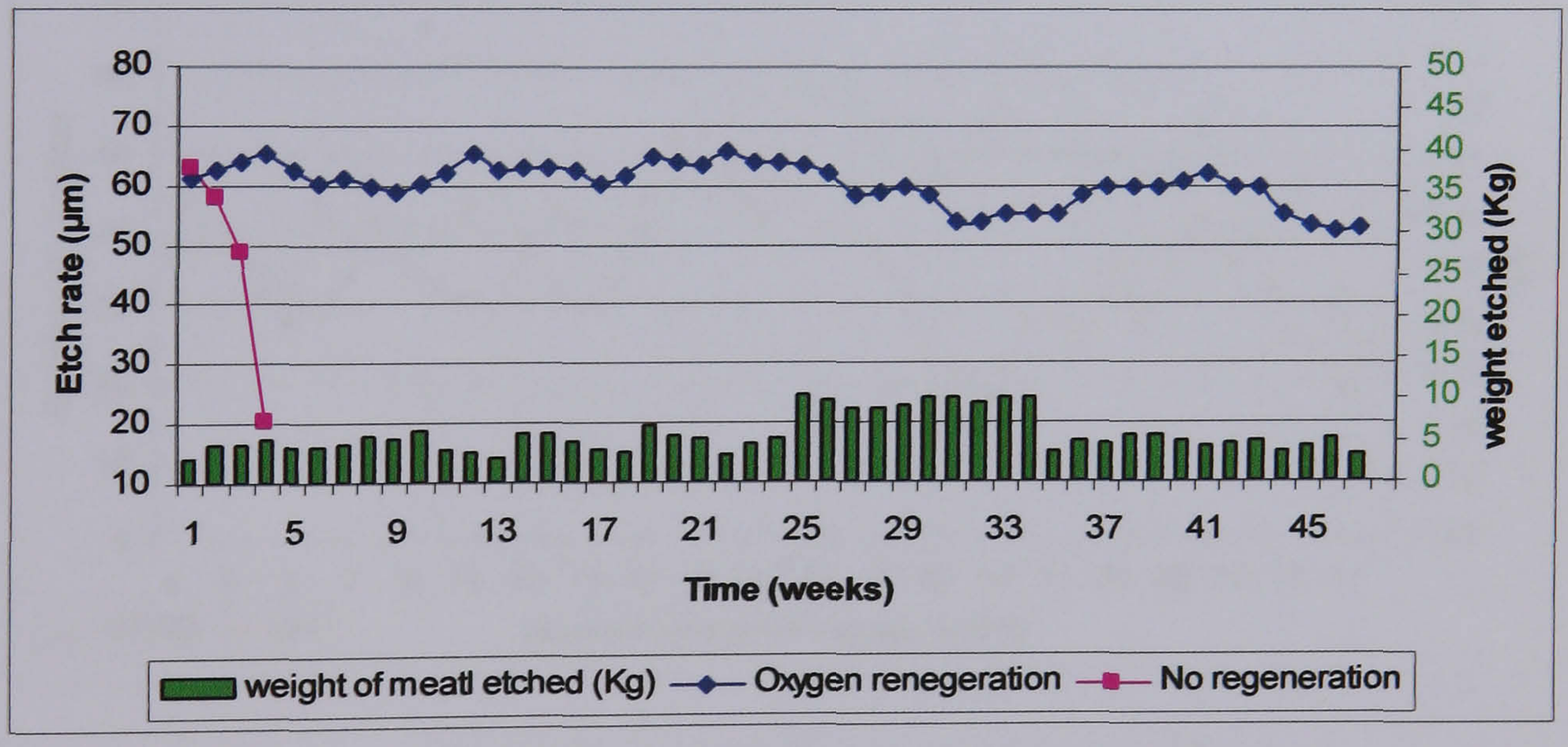


Figure A16.12 Etch rate and metal loading during extend trials (started Jan 2005), comparison to no regeneration also shown. Note drop in etch rate during weeks 41 to 45 this was due to increasing specific gravity of the etchant as shown in the previous chart.

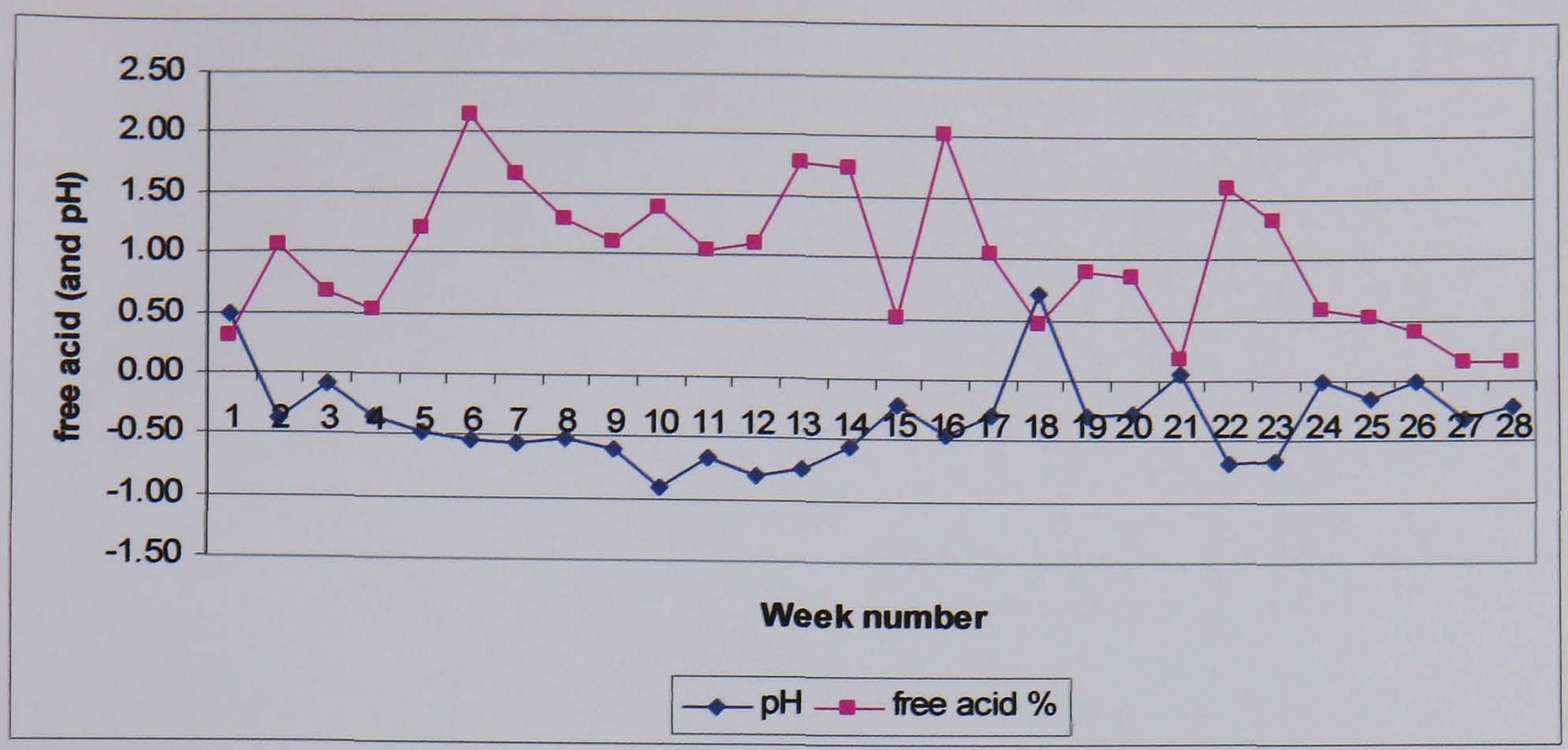


Figure A16.13 Free acid v lab titration for free acid. These are 'spot' results taken as specific times and days. They show no firm correlation between the titrated result and that obtained by pH measurement. *(Test started Jan 2005)*

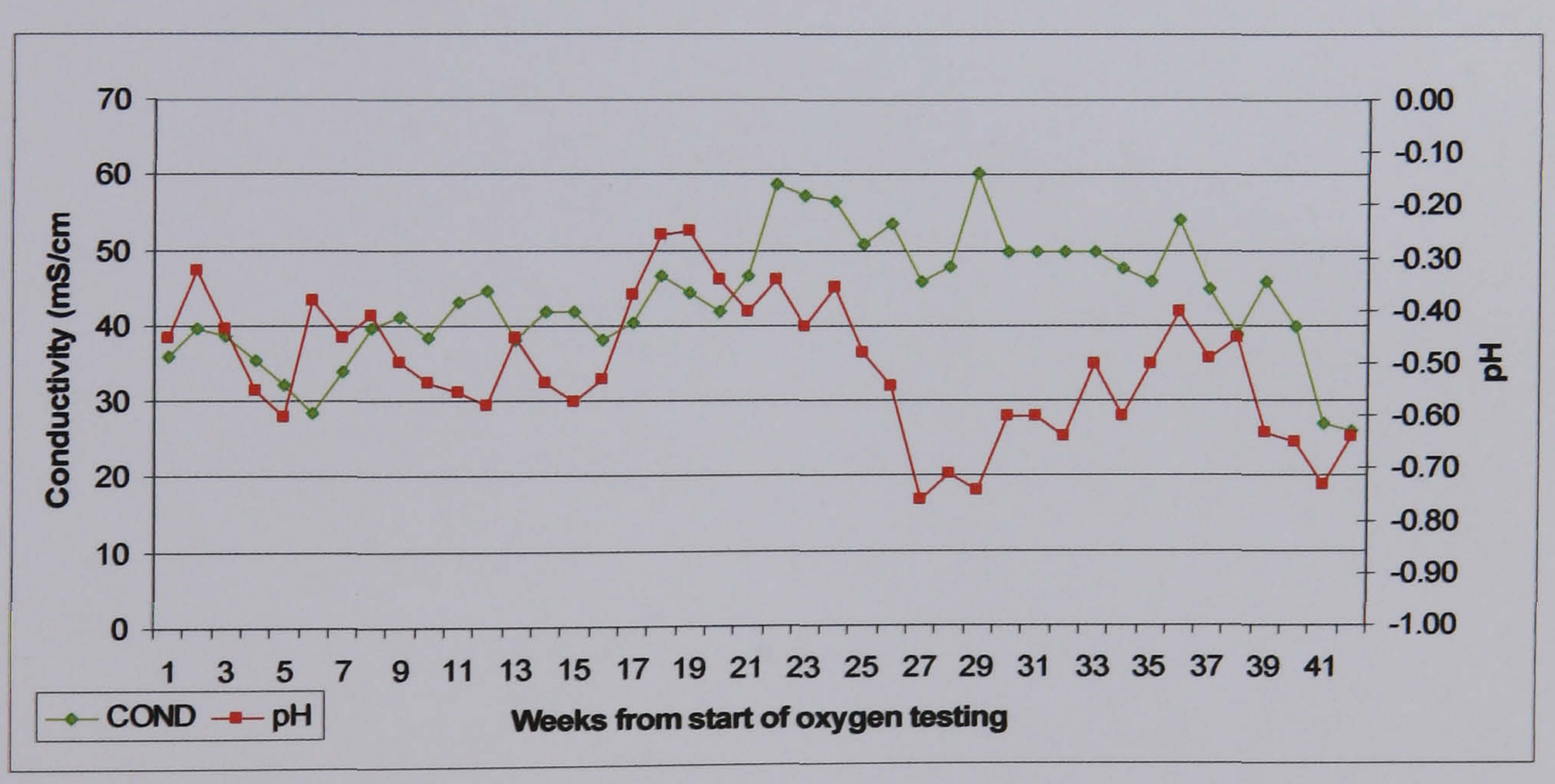


Figure A16.14 Conductivity v pH showing no form correlation. *(Test started Jan 2005)*